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Lyle Kay Matson
Iowa State University

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FURTHER STUDIES IN THE ELUTION OF COPPER AND NEODYMIUM FROM A CATION-EXCHANGE RESIN WITH AMMONIA-ETHYLENEDIAMINETETRAACETIC ACID SOLUTIONS

by

Lyle Kay Matson

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TABLE OF CONTENTS

INTRODUCTION

The group of elements with atomic numbers 39 and 57 through 71 are commonly known as the rare earths. At present the greatest demand for pure rare-earth elements, other than lanthanum, cerium, and perhaps neodymium, is for fundamental scientific research. Since the atoms of each of the respective rare-earth elements differ from each other primarily in the number of electrons contained in the shielded 4f subshell and the number of protons in the nucleus, their unique physical and chemical properties, such as ionic size, make them valuable tools for testing many of the theories which have been proposed in chemistry and physics.

The separation of the lanthanide elements from each other has long been a classic problem in chemistry. Because of the inherent similarities of the adjacent rare-earth ions in aqueous solution of a given oxidation state, most techniques not based upon oxidation or reduction are commonly slow, tedious, and fractional in character. Techniques involving more than a single oxidation state are rapid and yield pure products, but they are limited to a few members of the series. Prior to 1947 the separation of rare earths except for that of lanthanum and those having more than one oxidation state was so difficult and tedious that only small quantities were obtained. In recent years, however, ion-exchange techniques have been applied with great success to this separation problem and all of the rare earths are available in kilogram or larger quantities with a purity of 99.99 per cent or greater. Even though it is commercially more economical to use liquid-liquid extraction for rough separations of rare earths, it is still necessary to use the ion-exchange procedure in most cases to obtain the individual rare earths in high purity.

The ion-exchange methods which have proven most successful involve the use of an organic chelating agent in the eluant. The successful separation of the rare-earth elements by this method depends for the most part upon the differences in the stabilities of the complexes formed between the individual rare earths and the chelating agent.

The chelating agent generally used for the economical separation of the rare earths is ethylenediaminetetraacetic acid (EDTA). The retaining bed which has worked the best with EDTA is the pure cupric ion bed (1, 2).

As is often the case, during the early work on such a process when the product is in great demand, the technology resulting in the actual separation of the rare earths has advanced more rapidly than the theory of the ion-exchange elution mechanism. Approximate conditions have been worked out for the best separation of the rare earths; however, a more detailed knowledge of the elution system was desirable in order to determine the optimum conditions for the separation of rare-earth mixtures of various compositions.

In the separation of rare earths at this laboratory, it was found that ammonium was "leaking" from the eluant through the "pure" copper retaining bed. By keeping the copper retaining bed short and constantly supplying fresh copper retaining beds, the build-up of ammonium in the bed could be kept to a minimum and a stable system could be achieved. When the author investigated the elution of neodymium band behind a pure copper retaining resin bed, it was found that the ammonium ion leaked through and built up in the copper band in such a way that the band's equilibrium with the eluate was constantly shifting (3). This in turn causes the equilibrium between the resin and the solution phase of the rare-earth band to shift. The rate of transfer of materials at the various boundaries was so slow that the bands would not come to equilibrium or to a steady state by the time the band had traveled three band lengths. By using a homogeneous copper-ammonium-hydrogen band instead of the pure copper resin, it was possible to achieve "flat" equilibrium type neodymium bands in this distance. However, there was a tendency for the retaining bed to very slowly shift in composition. On the other hand, when a homogeneous copper-hydrogen resin was used rather than the pure copper retaining bed, the high concentration of the hydrogen in the copper-hydrogen band precipitated EDTA in the neodymium band which caused some difficulty. However, the copper-hydrogen band should lend itself to the formation of a stable equilibrium retaining band if the precipitation of the EDTA in the neodymium band could be overcome. In order to take advantage of the good retaining characteristics of the copper-hydrogen band and to remove the precipitation difficulty, a short copper-ammonium-hydrogen band was used between the copper-hydrogen retaining bed and the rare-earth band.

The purposes of this thesis are to investigate quantitatively the use of a buffering band interposed between the retaining bed and the rare-earth band and to study the mass transport of the atomic species across the band boundaries. It was hoped that conditions could be established by using appropriate buffer bands so that flat-type elution curves could be obtained, and at the same time the composition of the final retaining bed could be varied with respect to a given eluant. This objective was achieved. Also, it should be possible to calculate the behavior of such a systen theoretically by means of the mass-action, charge-balance, and material-balance equations. The possibility of transporting atomic species through the boundaries gives the system an extra degree of freedom and a corresponding greater flexibility. This theory is developed in the thesis.

Since the apparent equilibrium constants involved in the copper-ammonium-hydrogen and neodymium-ammonium-hydrogen bands are needed in the theory, some rough equilibrium studies were made for the sake of comparison.

It was hoped that the more precise knowledge gained about this elution system would be helpful in the study of other elution systems.

The resin used in these investigations was a sulfonated polystyrene-divinylbenzene co-polymer. Its sole ion-active groups were the sulfonic acid groups. The resin phase of the cation-exchange system designated above consists essentially of a porous hydrocarbon network linked and crosslinked by short aliphatic chains.

When a resin is initially placed in water, the polymer network expands as the ions become hydrated and as water is adsorbed due to the osmotic forces. The extent of the swelling will finally be limited by the network which hold the polymer together. A considerable amount of work has been reported in regard to the volumes of resin observed under various conditions (4, 5, 6, 7, 8, 9). The volume occupied by the resin depends on the ions within the resin, the type of resin, and the concentration of the solution in contact with the resin. However, the change in volume with concentration of the external solution is quite small when this concentration of the electrolyte is low.

Solvent and neutral molecules can freely migrate into and through the polymeric network. Positive ions from an external solution can diffuse through the resin as long as electrical neutrality is maintained. Whenever a cation enters the resin an equivalent amount of positive ion must be displaced or it must be accompanied by an equivalent amount of anion. However, since the activity of the salt within the resin must equal the activity of the salt in the external solution, the high concentration of cations within the resin will effectively prevent the solution anions from entering the resin phase when the ionic strength of the external solution is low (Donnan equilibrium).

When a wet swollen hydrogen form resin is immersed in a solution containing ammonium chloride, an important reaction takes place in that an exchange would occur with hydrogen ion being displaced from the exchanger by an equivalent amount of ammonium ions. This exchange phenomenon is the most useful property exhibited by these high molecular weight polymers.

A metathetical reaction can be written for the cations in the exchange equilibrium,

$$n\,A_o^{+m} + m\,B_i^{+n} \rightleftharpoons n\,A_i^{+m} + m\,B_o^{+n} \qquad (1)$$

where the subscripts "o" and "i" refer to the ions being outside and inside the resin phase. The selectivity coefficient K' has been defined as follows:

$$K' = \left(\frac{A_i^{+m}}{A_o^{+m}}\right)^n \left(\frac{B_o^{+n}}{B_i^{+n}}\right)^m \qquad (2)$$

where the quantities are the appropriate stoichiometric concentrations of the ions in the two equilibrium phases. This is really a mass-action constant or an apparent equilibrium constant where the terms are expressed in concentrations rather than activities. This constant will change somewhat with the ionic concentration of the eluate and the composition of the resin since it is a function of the activity coefficients of the ions and the true equilibrium constant. This constant is best determined experimentally for the conditions involved.

The selectivity coefficient as defined has little meaning unless accompanied by a statement as to the composition of the resin (9, 10, 11, 12, 13, 14, 15, 16). Other factors remaining constant, the selectivity coefficient diminishes slightly with the ionic strength of the external solution when it is dilute (13, 16, 17). There have been reports of actual reversal of the selectivity at very high concentration. While the total ionic strength was a minor variable with the uni-univalent systems, it may or may not be a major variable if the exchanges involve ions of differing charges (18, 19, 20, 21). There is general agreement that the dependence of the selectivity coefficient on temperature is small (13, 14, 17, 22, 23).

The more highly charged ions are preferred by the resin over those of lesser charge. For ions of the same charge, those with the smaller hydrated radii have the greater affinity for the resin (9, 22, 23, 24).

There are a number of conflicting views on how the true thermodynamic constants should be expressed and on the relationship between the apparent constant and the true thermodynamic constant (25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36). The mathematical developments of the various theories are quite different. Even though the mathematical development of the theory is the same, there may be disagreement over which of the terms in the development are most important. For example, there is disagreement over the importance of the osmotic pressure inside the resin for the Gibbs-Donnan development. Therefore, it is better to determine the selectivity coefficient under the conditions where the coefficient will be used rather than to try to calculate the coefficient from data obtained under other conditions.

In addition to the selectivity coefficients, the four stability constants of EDTA are required in the mathematical treatment of the neodymium-ammonium-hydrogen bands and copper-hydrogen bands. Therefore, it was necessary to determine these constants at the appropriate ionic strength (0.015-0.02).

REVIEW OF LITERATURE

One problem in which ion exchange has been very useful is the separation of the rare earths. The early method of separating the rare earths by means of ion exchange was developed at Ames (37, 38, 39, 40, 41) and elsewhere (42, 43, 44, 45, 46, 47, 48, 49). This method consisted of eluting the rare earths down an ion-exchange column which was initially in the hydrogen cycle with an approximately 5 per cent citric acid-ammonium citrate solution. The elution curve of each individual rare earth was "bell shaped". The different rare earths moved down the column at different rates so that they gradually separated from each other. However, to separate macro quantities of the rare earths the bands had to travel a great distance and a considerable fraction of the bands overlapped. This method was particularly successful for separating radioactive tracers where adsorbed bands were very short.

Spedding and his co-workers conducted numerous experiments in which a rare-earth band was eluted down a resin bed with a 0.1 per cent citric acid solution, adjusted to a pH between 5.0 and 8.0 with ammonium hydroxide (50, 51, 52, 53, 54, 55). A resin bed in the hydrogen form was used to retain the rare-earth band. If several individual rare-earth species are present in the originally absorbed band, they tend to separate into individual bands which are compact and follow one another "head to tail" as the total band is eluted down the column. After an equilibrium state has been reached, each rare earth has a rectangular elution curve with fairly sharp boundaries between each pair of adjacent rare earths. This elution system will be discussed in the Theoretical Discussion along with the system studied in this thesis (56, 57).

An application of the theoretical and practical knowledge of the operation of ion-exchange columns was published by Spedding et al. (58, 59). One of these, a practical separation of the nitrogen isotopes N^{14} and N^{15}, has been brought about by methods similar in principle to those used in the rare earth separations. Ammonium hydroxide is reacted with a hydrogen ion bed within a column to form an ammonium ion band. This band is eluted down hydrogen-ion resin beds with an eluting solution of sodium hydroxide. The sodium hydroxide reacts with the ammonium ion on the resin to form ammonium hydroxide and sodium saturated resin. Then, the ammonium hydroxide in solution moves down the ammonium band and reacts with the hydrogen ion on the resin at the leading edge of the band to form adsorbed ammonium ion. Since the equilibrium constants are large for both the reaction at the leading boundary and the rear boundary, these boundaries are sharp and the ammonium band is well defined. The two isotopes of nitrogen are differentiated because the distribution coefficients of these two isotopes are slightly different for this system. $N^{15}H_4^+$ concentrates at the back end of the adsorbed band and $N^{14}H_4^+$ at the front end of the adsorbed band.

Several articles have been written by Spedding, Schwarzenbach, Powell, and Wheelwright on the stability of the rare-earth-EDTA complexes and the separation of the rare earths by ion exchange using EDTA. Preliminary studies (60) indicated that EDTA could be used in the separation of the rare earths. Then stability constants of the complexes formed between the rare-earth metal ions and the anion of ethylenediaminetetraacetic acid were measured at a temperature of 20° C and the ionic strength of 0.1 by two independent methods (61, 62). The two methods were shown to supplement each other, one being more accurate for the lighter rare earths and the second method more accurate for the heavy rare earths. The first, the potentiometric method, involved the formation constants of copper with the anion of ethylenediaminetetraacetic acid and of copper with the trihydrochloride of β, β', β''-triaminotriethyleneamine. The second method utilized the polarographic determination of the amount of free copper in the presence of both the copper and rare earth-EDTA complexes.

In other studies by Spedding <u>et al</u>., some success was obtained using a ferric ion in the retaining bed (63). However, experiments with long resin beds, using solutions of EDTA, have indicated that ferric ions are not the most desirable for use in the retaining bed. When iron was used, it was found that the pH range was limited. If the solution were too acidic, the acid EDTA tended to precipitate in the interstices of the resin bed, and if it were too basic, hydrous ferric hydroxide clogged the resin pores.

It was obvious that some ion having a more soluble hydroxide than ferric ion would be a more desirable choice for the retaining ion in this elution. Consideration of the stability constants for the EDTA complexes of the rare earths and other metals showed that the cupric ion should serve to retain a number of the rare earths. Since, in general, ions with a plus three charge have a greater affinity for the resin than ions having a plus two charge, the cupric ion might retain more rare earths than indicated when only the stability constants are considered. In fact, Spedding *et al*. (64) have shown that cupric ion can be used to retain all of the rare earths. Their method consisted of eluting a band of mixed rare earths adsorbed on a cation-exchange resin through a second cation-exchange bed in the cupric state using an ammonia buffered solution of EDTA as the eluant. It was found that gram quantities of pure heavy rare earths could be obtained in a few days. This method has been expanded so that 1,000 pounds of rare earths can be separated with one elution.

Near optimum conditions have now been established. It is recommended that rare earth separations be made with 0.015 molar EDTA at pH 8.4 (2, 65). With the larger equilibrium constants for the exchange of adjacent rare earths, this type of elution gave a cleaner cut separation with less overlap of bands than the citrate method and the bands attained equilibrium within a shorter distance.

Most adjacent pairs of rare earths can be separated by eluting a distance equal to the length of the adsorbed band, and the more difficult pairs, Sm-Gd, Tb-Y, Y-Dy, and Yb-Lu, can be resolved by eluting approximately three times the length of the adsorbed band. Also considerably less eluant is required for a given elution when EDTA is used in place of citrate. The principal disadvantages are that the cost of the chemicals is somewhat higher, the eluant is difficult to recycle, and the pH ranges and eluant concentrations are more critical than with citric acid. Too low a pH in the eluant results in the precipitation of acid EDTA, and too high a pH causes the precipitation of Cu_2(EDTA). As the EDTA concentration in the eluant is increased, the allowable pH range becomes narrower. Also, at high pH values, Lu, Yb, and Tm are not completely retained by the cupric ion and losses may occur unless precautions are taken.

Several experiments were performed in which neodymium bands were eluted behind copper bands with dilute ammonia-EDTA solutions by the author at Ames Laboratory (3). Also, a few other experiments were performed eluting only copper bands. If a certain amount of ammonium and hydrogen were mixed homogeneously with the copper in the resin, flat elution curves were obtained. However, when a neodymium band is inserted above this copper band there is slight tendency for the copper band to shift in composition. This tendency of the retaining bed to shift composition made it desirable to undertake further studies of the factors which influence such a system.

RESEARCH AND RESULTS OF COLUMN ELUTIONS

Materials

The resin used in the following experiments was a sulfonated polystyrene-divinylbenzene type which was purchased from Rohm and Haas of Philadelphia, Pennsylvania. It was labeled as Amberlite IR-120 and was a 40 to 50 mesh resin. The neodymium was supplied as the oxide by the rare-earth separation group at the Ames Laboratory of the Atomic Energy Commission. Its purity was greater than 99.99 per cent.

The ethylenediaminetetraacetic acid (H_4Y), which was supplied by the rare-earth separation group, was purchased from Geigy Chemical Corporation of Yonkers, New York. In order to remove the slight amount of sodium and heavy metals that might be in the reagent, the H_4Y was dissolved in a minimum amount of concentrated ammonium hydroxide. The resulting solution was filtered and diluted. The H_4Y was precipitated using a minimum amount of hydrochloric acid and washed with deionized water. Then the H_4Y was converted to a concentrated solution of $(NH_4)_2H_2Y$ by adding deionized water and ammonium hydroxide. The $(NH_4)_2H_2Y$ was precipitated by adding 95 per cent ethyl alcohol, filtered, washed again with 95 per cent ethyl alcohol, and died in the oven at 80° C.

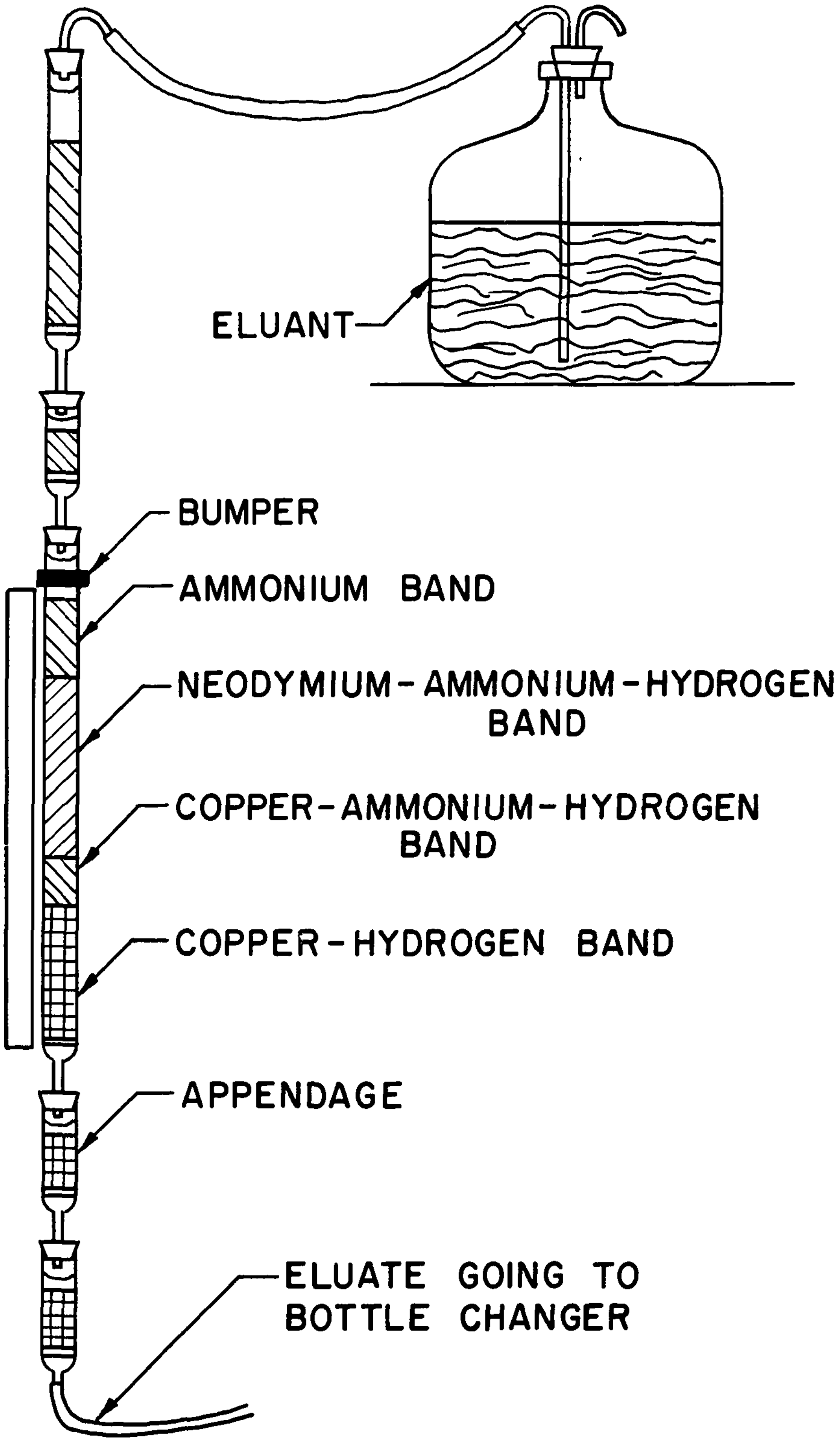
Baker and Adamson C. P. reagent or E. I. duPont de Nemours reagent hydrochloric acid was used for preparation of the neodymium chloride solutions from the oxide and for preparation of the various other solutions, and Baker and Adamson C. P. reagent or duPont reagent ammonium hydroxide was used in preparing the eluant solutions. All other chemicals used, such as the ammonium chloride, cupric sulfate, sodium hydroxide, and oxalic acid, were "Baker Analyzed" reagent or Fisher "Certified" reagent grade.

The laboratory distilled water was passed through glass-wool filters and a cation- and anion-exchange deionizer in order to remove any iron oxide and salts. This water was used in preparing all of the solutions.

Apparatus

A diagram of the apparatus is shown in Figure 1. The container for the eluant was a 10-gallon carboy. The long column was approximately 130 centimeters in length and was filled to a height of approximately 110 centimeters with resin, while the medium-sized column was approximately 50 centimeters in length and contained approximately 35 centimeters of resin. The appendages were approximately 14 centimeters in length and contained about 3 centimeters of resin. The exact length of the resin bed depended on the cationic composition of the resin, the solution with which the resin was in contact, and the extent to which the resin had packed. Each column and appendage had an inside diameter of approxi-

Figure 1. Schematic drawing of apparatus


ELUANT
BUMPER
AMMONIUM BAND
NEODYMIUM - AMMONIUM - HYDROGEN BAND
COPPER - AMMONIUM - HYDROGEN BAND
COPPER - HYDROGEN BAND
APPENDAGE
ELUATE GOING TO BOTTLE CHANGER

mately 2.2 centimeters.

A short piece of Tygon tubing with a screw clamp in the middle was attached to the bottom of each column or appendage, and a medicine dropper type tip was inserted into the other end of the Tygon tubing so that the eluate from the column could be either collected in a volumetric flask or passed by means of Tygon tubing to another column or appendage. A rubber stopper with a glass tube through the center was inserted into the top of each column or appendage so that the column and appendages could be attached in series by means of Tygon tubing. A bumper was attached securely at the top of the long column so that all of the measurements could be made conveniently from the same reference point.

Methods of Analysis

The analytical method used to determine neodymium consisted of precipitating the neodymium from an aliquot of the unknown solution, which was near the boiling point, with an excess of a saturated solution of oxalic acid. The precipitated sample was allowed to cool and then filtered with Schleicher and Schuell No. 589 Blue Ribbon paper. The precipitate was washed with dilute oxalic acid and transferred to a porcelain crucible which had been brought to constant weight. Then the precipitate was ignited in a muffle furnace and held overnight at approximately 850° C. The sample was removed from the furance, cooled for five hours in a desiccator, and weighed. From the difference in weight between the crucible plus sample and the empty crucible, the weight of the neodymium oxide was obtained.

If there were sodium ions in the solution, the procedure was modified. The neodymium oxalate was digested near boiling for two hours before filtering the precipitate from the solution. The precipitate was washed with one per cent ammonium chloride solution containing a small amount of oxalic acid. The precipitate was washed into a beaker with deionized water and dissolved by adding a minimum amount of concentrated hydrochloric acid. Then the solution was diluted and neutralized with ammonium hydroxide until only slightly acidic. After a slight excess of oxalic acid was added to the solution, the neodymium oxalate was digested again for two hours. The precipitate was filtered, ignited, and weighed as indicated above.

The concentration of the ammonium ion was determined by the Kjeldahl procedure (66). An aliquot of the solution was pipetted into a distillation apparatus and diluted to a volume of about 200 milliliters. Approximately 50 milliliters of a 50 per cent sodium hydroxide solution were added, and the ammonia was boiled off through a spray trap, condensed by means of a glass condenser into a receiver containing an indicator-boric acid solution, and titrated with a standard solution of hydrochloric acid. The original 250 milliliters of solution were boiled down to approximately 70 milliliters. The indicator-boric acid solution was prepared by diluting 10 milliliters of a concentrated methyl purple indicator solution, which was supplied by Fleisher Chemical Company, and 30 grams of boric acid crystals to one liter. Twenty milliliters of this solution were added to each flask used to collect the ammonia. It was verified that the presence of EDTA in the initial aliquot did not change the value of the blank as determined by this procedure.

The total EDTA concentration in the eluant was determined by titrating a known amount of a standard zinc chloride solution with the unknown solution using Eriochrome Black T as the indicator. The standard zinc chloride solution was buffered with 10 milliliters of an ammonia-ammonium chloride solution. The buffer solution was prepared by diluting 6.75 grams of ammonium chloride and 57 milliliters of concentrated ammonium hydroxide to 100 milliliters (67).

The total copper concentration was determined by the general method (66) of plating out pure copper metal electrolytically on a platinum screen. The cathode and anode were cleaned with six normal nitric acid, washed, and heated to redness in a flame. The cathode was allowed to cool to room temperature and weighed. An aliquot of the unknown solution was placed in a 250 milliliter beaker, and the electrolysis was performed at a potential of approximately two volts using a commercial electrolytic apparatus. This apparatus had a rotating platinum anode which stirred the solution during the analysis. About one gram of ammonium nitrate was added to the solution to improve the copper deposit. Water was added to the beaker after a couple of hours. If no new deposit formed after about 15 minutes, the motor was turned off and the electrodes were thoroughly washed, using a wash bottle, as they were removed slowly from the solution. After the current was turned off, the cathode was removed, immersed in a beaker of water, and rinsed twice with alcohol to remove the water. Then the cathode was heated in an oven at 100° C for two or three minutes, cooled to room temperature, and weighed.

The excess copper in the solution containing EDTA was titrated using a standard solution of $(NH_4)_2H_2Y$ according to the method described by Schwarzenbach (68). The aliquot of the solution to be analyzed was buffered by adding a small amount of ammonium chloride and a one molar ammonium hydroxide solution. The ammonium hydroxide solution was added dropwise until a pH of 7.6 was attained according to the pH meter. Several drops of a freshly saturated solution of murexide were added to the solution, and the solution was titrated with standard $(NH_4)_2H_2Y$ until the color changed from yellow to violet. This procedure determined the molar concentration of the copper (Cu_E) in excess of the one to one complex of copper with EDTA in the unknown solution. If EDTA was present in excess, the procedure was the same except that the excess EDTA (Y_E) was titrated with a standard solution of copper sulfate and the solution turned from violet to yellow at the end point.

The excess EDTA in a solution containing neodymium was titrated with standard neodymium chloride solution according to the method described by Schwarzenbach (68). An aliquot of the solution to be analyzed was buffered by adding a small amount of ammonium chloride and a one molar ammonium hydroxide solution. During the titration, the ammonium hydroxide solution was added dropwise to maintain a pH of 7.0 or slightly above according to the pH meter. A small amount of solid Eriochrome Black T, diluted in crystalline sodium chloride, was added to the solution, and the solution was titrated with standard neodymium chloride solution. The color changed from blue to red at the end point. This method determined the molar concentration of the EDTA (Y_E) in excess of the one to one complex of EDTA with neodymium in the unknown solution.

If the solution had a composition of essentially H_2CuY, which was true for the eluate samples from the copper-hydrogen band, the total replaceable hydrogen-ion concentration (H_T) was determined in the following manner. Several drops of phenol red indicator were added to an aliquot of the solution, and the solution was titrated with a standard potassium hydroxide solution. The color of the solution changed from green to purple at the end point. Solutions containing excess EDTA were corrected for the formation of the HY^{-3} at the end point.

The hydrogen ion in a solution approximately three molar in sodium chloride and containing much smaller amounts of neodymium chloride, ammonium chloride, and hydrochloric acid was titrated with the standard potassium hydroxide solution. Methyl purple indicator was the indicator which was used since the ammonium chloride in the solution determined the pH at the end point, and the color changed from green to purple.

The total replaceable hydrogen in the eluate samples from the copper-ammonium-hydrogen band (see page 29) was titrated with the standard potassium hydroxide solution using a pH meter to potentiometrically detect the end point which was at a pH of approximately 4.6. The hydrogen ion in a solution approximately two molar in sodium chloride and containing much smaller amounts of copper chloride, ammonium chloride, and hydrochloric acid was titrated with the standard potassium hydroxide solution using a pH meter to potentiometrically detect the end point. This solution was obtained when a two molar sodium chloride solution was passed slowly through an appendage to remove all of the ions adsorbed on the resin.

Preparation of Eluant

The desired amount of a standard $(NH_4)_2H_2Y$ stock solution and slightly less than the desired amount of concentrated ammonium hydroxide were added to a calibrated carboy and the carboy contents were diluted to the mark and mixed. From the pH of the solution and a plot of pH versus eluant composition, the amount of ammonium hydroxide required to obtain the desired ammonium concentration was calculated. After this quantity of ammonium hydroxide was added and the solution mixed with a large stirrer for 15 minutes, the concentrations of the ammonium and the EDTA were determined as indicated in the previous section.

Preparation of Resin Beds

The neodymium-ammonium-hydrogen band, which was to be eluted down the column, was prepared by converting the hydrogen-form resin placed in the column to the approximate desired composition. A homogeneous solution of neodymium chloride, ammonium chloride, and hydrochloric acid was passed through the column to convert the resin to the desired form. The expected composition of the neodymium-ammonium-hydrogen band was calculated from the theory of the elution. The composition of the solution necessary to obtain this resin was calculated from the approximate ion-exchange constants (16). A pure rare-earth band could have been used. However, this band which is far from the equilibrium state would have disrupted the other bands initially; and a larger volume of eluant and a longer retaining bed would have been necessary to achieve the equilibrium condition. After the resin in the column has achieved equilibrium with the mixed solution, the excess solution above the resin was removed and the solution surrounding the resin was removed by passing deionized water through the column.

A copper-ammonium-hydrogen band of the approximate composition to be expected in the elution was prepared by passing a solution of copper sulfate, ammonium chloride, and hydrochloric acid through the second column indicated in Figure 1 (3). The purpose of this short bed was to prevent the high concentration of hydrogen in the copper-hydrogen bed from getting into the neodymium-ammonium-hydrogen band and precipitating EDTA. The excess solution was again removed from the top of the resin bed and deionized water was passed through the column to remove the excess salts in the resin.

The copper-hydrogen band was prepared in a slightly different way than neodymium-ammonium-hydrogen and copper-ammonium-hydrogen bands. A resin completely saturated with cupric ions was prepared by passing an excess of cupric sulfate through some hydrogen-form resin. After the resin was thoroughly washed, it was air dried to a practically constant weight. Then this air-dried resin was placed in a bottle and mixed thoroughly by continually inverting the bottle.

The number of equivalents of copper per gram of resin was determined by weighing some resin into a small column and stripping the copper into a volumetric flask with a concentrated sodium sulfate solution. After the contents of the flask were diluted to volume, aliquots were analyzed for copper by the electrolytic method. An air-dried, hydrogen-form resin was prepared in the same way. However, hydrochloric acid was used to saturate the resin and a concentrated solution of sodium chloride was used to strip the hydrogen ion from a weighed sample of the resin into a volumetric flask. After the contents of the flask were diluted to volume, aliquots were titrated with a standard potassium hydroxide solution in order to determine the quantity of hydrogen on the resin.

The proper amount of copper-form resin and hydrogen-form resin were weighed into an Erlenmeyer flask to give resin of the desired composition. Deionized water was added to make up for the water which would be adsorbed by the resin in swelling to its equilibrium state. A dilute solution of copper sulfate and hydrochloric acid, which would be approximately in equilibrium with the resin, was added to the flask. After the resin and solution were mixed with a magnetic stirrer for four days, the solution was suction filtered and washed from the resin into a volumetric flask. After the equilibrium solution was analyzed, the resin composition was calculated from the sum of the copper in the initial air-dried resin and solution added to the flask minus the copper in the solution washed from the resin. The equivalents of hydrogen in the final resin sample may be calculated in the same manner. Thus, it was now certain that the resin was homogeneous and that its composition was known quite accurately.

Samples containing approximately the same quantity of resin were placed in several appendages and the remaining portion of resin was placed in the long column.

Observations and Measurement of Boundaries between the Bands

After the columns and the appendages were connected in series with Tygon tubing as shown in Figure 1, the eluant was started through the series at the flow rate of one milliliter per minute. The eluate was collected in volumetric flasks by means of an automatic bottle changer. The positions of the boundaries between the ammonium, the neodymium-ammonium-hydrogen, the copper-ammonium-hydrogen, and the copper-hydrogen bands were recorded twice a day at approximately equal time intervals and the amount of eluate was also noted at these times. Since there was a slight change in the length of the resin bed as the resin changed composition, the position of the top of the resin bed was also noted at these times. The distances measured from the bumper to a boundary were corrected for the non-uniform diameter of the column. See Figures 2 and 4 for the plots of the position of the boundaries versus the total volume of eluate collected.

Analysis of Eluate Samples

The pH's of all of the eluate samples in the volumetric flasks were determined using a Beckman glass-electrode pH meter. The pH meter was standardized against the Beckman pH 4 buffer and checked against the Beckman pH 7 buffer.

The total replaceable hydrogen was determined for both the copper-hydrogen band and the copper-ammonium-hydrogen band. The ammonium concentration was determined for the copper-ammonium-hydrogen band and neodymium-ammonium-hydrogen band eluates. The total concentration of excess copper or excess EDTA was determined by titration depending on which substance was in excess in the eluate sample of the copper-hydrogen band and the concentration of the excess copper was determined for the copper-ammonium-hydrogen band eluates. The total neodymium concentration and the excess EDTA concentration were also determined for each eluate sample from the neodymium band. See Figures 3 and 5 for the plots of the concentrations of various species versus total volume of eluate at the time the sample was collected.

Figure 2. Distances of the three boundaries from the bumper versus the total eluate collected at the time of measurement for a retaining bed which is nearly compatible with eluent (elution 27)

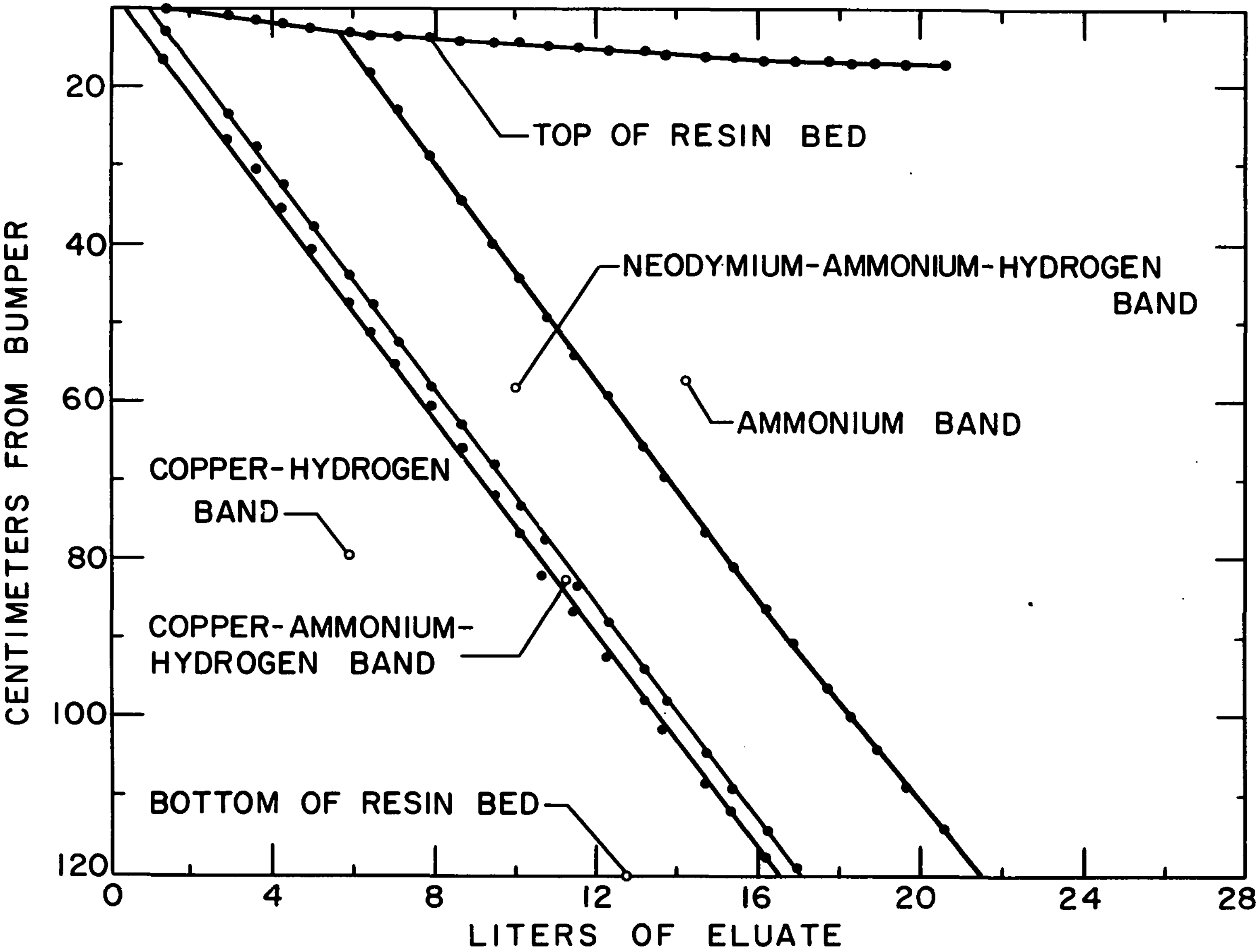
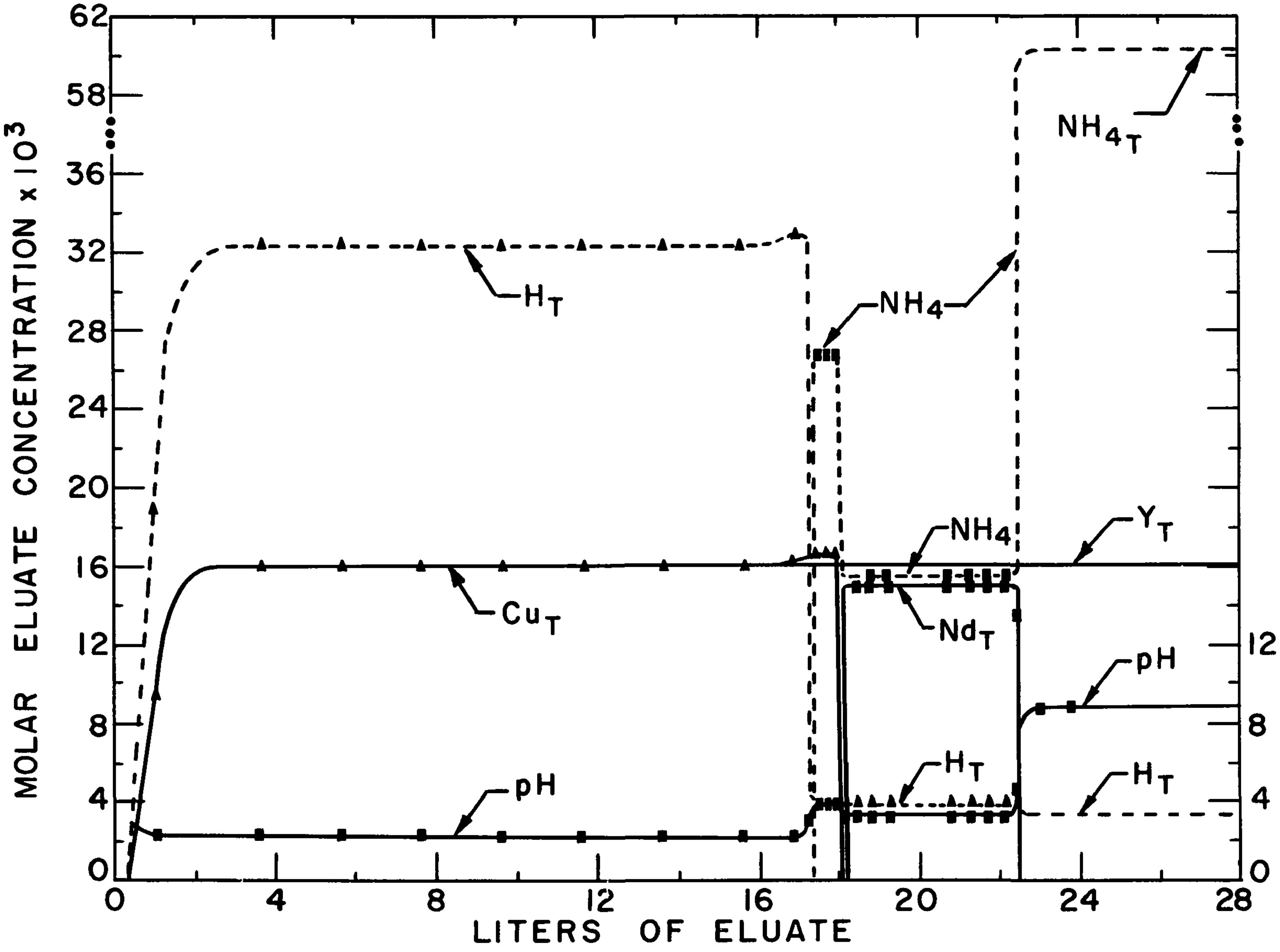

TOP OF RESIN BED
NEODYMIUM-AMMONIUM-HYDROGEN BAND
AMMONIUM BAND
COPPER-HYDROGEN BAND
COPPER-AMMONIUM-HYDROGEN BAND
BOTTOM OF RESIN BED
CENTIMETERS FROM BUMPER
20
40
60
80
100
120
0
4
8
12
16
20
24
28
LITERS OF ELUATE

Figure 3. The composition of the eluate sample versus the total volume of the eluate at the time the sample was collected for a retaining bed which is nearly compatible with the eluant (elution 27)



MOLAR ELUATE CONCENTRATION x 10^3
LITERS OF ELUATE
0
4
8
12
16
20
24
28
32
36
58
62
0
4
8
12
16
20
24
28
0
4
8
12
H_T
NH_4
NH_{4T}
NH_4
Y_T
Cu_T
Nd_T
pH
pH
H_T
H_T

Figure 4. Distance of the three boundaries from the bumper versus the total eluate collected at the time of measurement for a retaining bed which is not compatible with the eluant (elution 29)

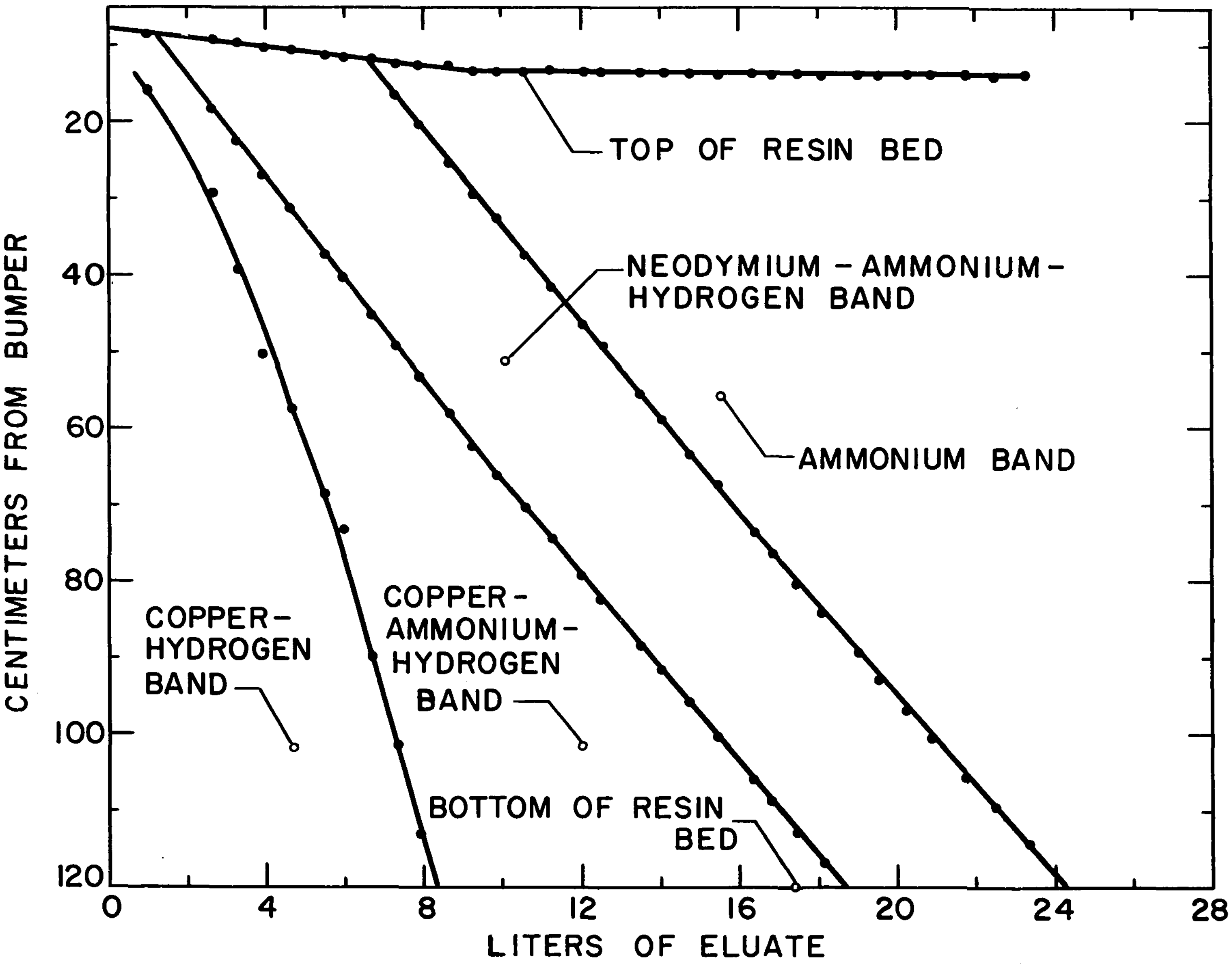
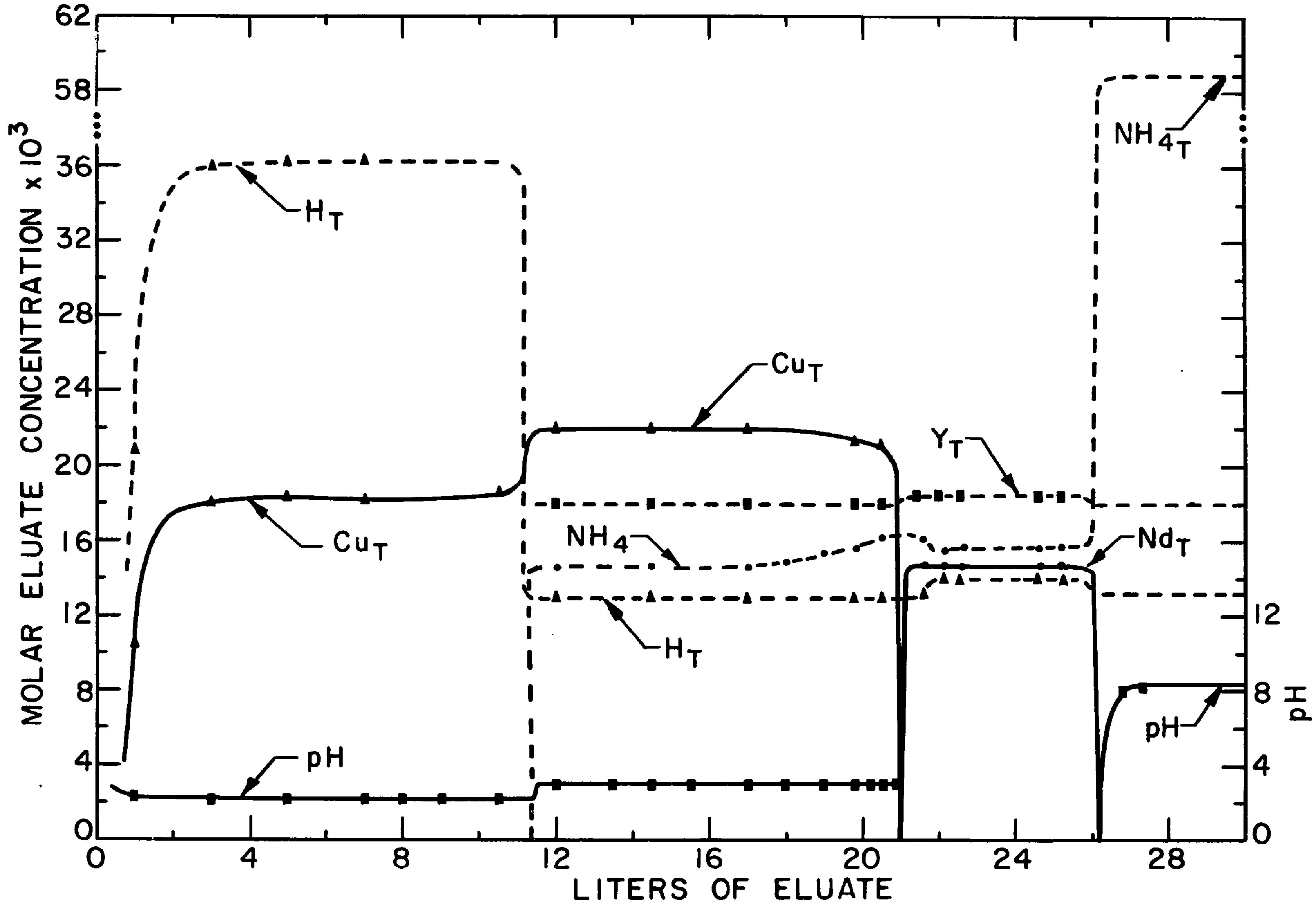

TOP OF RESIN BED
NEODYMIUM - AMMONIUM - HYDROGEN BAND
AMMONIUM BAND
COPPER - HYDROGEN BAND
COPPER - AMMONIUM - HYDROGEN BAND
BOTTOM OF RESIN BED
CENTIMETERS FROM BUMPER
20
40
60
80
100
120
0
4
8
12
16
20
24
28
LITERS OF ELUATE

Figure 5. The composition of the eluate versus the total volume of eluate at the time the sample was collected for a retaining bed which is not compatible with the eluant (elution 29)


MOLAR ELUATE CONCENTRATION x 10^3
62
58
36
32
28
24
20
16
12
8
4
0
LITERS OF ELUATE
0
4
8
12
16
20
24
28
pH
12
8
4
0
H_T
Cu_T
pH
Cu_T
Y_T
NH_4
H_T
Nd_T
NH_{4T}
pH

Analysis of Resin Samples

Each operation of preparing the beds, eluting the neodymium band down the complete set of beds, and analyzing the solution and resin samples was called a run. Results from several of the more important runs are recorded in Table 1. In the case of runs 27 and 28, there were two appendages below the long column and these appendages were removed when approximately half of the neodymium band remained on the long column. The large column was then connected directly to the bottle changer by means of the Tygon tubing. The elution was continued until the neodymium band was completely removed from the long column.

The run 29 had four appendages rather than two. The bottom appendage was removed when three-fourths of the copper-ammonium-hydrogen band remained on the long column and the second appendage from the bottom was removed when one-half of the copper-ammonium-hydrogen band remained on the long column. The remaining two appendages were removed from the middle of the neodymium band as in runs 27 and 28.

After the appendages were washed with deionized water, the ions in the various appendages were stripped into separate volumetric flasks with a concentrated sodium chloride solution. The contents of the volumetric flasks were diluted to volume, aliquots were analyzed for the particular ions, and the equivalent fractions of neodymium (E_{Nd}), ammonium

Table 1. Column data

		Run no.		
		27	28	29
Ammonium band	$\bar{Y}_T$	0.015902	0.01146	0.018624
	$\overline{NH_4}_T$	0.06017	0.03774	0.05887
	$\bar{H}_T$	0.00344	0.00810	0.01323
	$\overline{NH_4}_T/\bar{Y}_T$	3.784	3.293	3.266
	pH	8.85	8.40	8.41
	E_{NH_4}	1.00	1.00	1.00
Neodymium-ammonium-hydrogen band	Y_T	0.016074	0.011545	0.018515
	Nd_T	0.014997	0.00842	0.01478
	NH_4	0.015485	0.01233	0.01574
	H_T	0.003820	0.00857	0.01398
	Y_E	0.0010770	0.003120	0.003735
	pH	3.25	3.24	--
	E_{Nd}	0.7416	0.6638	0.8240
	E_{NH_4}	0.2512	0.3254	0.1594
	E_H	0.00716	0.01073	0.01662
Copper-hydrogen-ammonium band	Y_T	(0.01590)	(0.01146)	0.01789
	Cu_E	0.00076	0.00026	0.00408
	NH_4	(0.02668)	(0.01377)	0.01468
	Cu_T	(0.01666)	(0.01172)	0.02197
	H_T	(0.00360)	(0.00863)	0.01294
	pH	3.86	3.16	3.07
	E_{Cu}	(0.556)	(0.621)	0.8436
	E_{NH_4}	(0.441)	(0.365)	0.1510
	E_H	(0.0027)	(0.014)	0.0053
Copper-hydrogen band	Y_T	0.01607	0.01151	0.01818
	Cu_T	0.01599	0.01148	0.01823
	H_T	0.03228	0.02308	0.03626
	Cu_E	--	--	0.00005
	Y_E	0.00008	0.00003	--
	pH	2.16	2.25	2.13
	E_{Cu}	0.5275	0.6064	0.7583
	E_H	0.4725	0.3936	0.2417

(E_{NH_4}), and hydrogen (E_H) were calculated for the resin from the neodymium band. The equivalent fraction of copper rather than neodymium was calculated for the copper-ammonium-hydrogen band. The equivalent fraction is defined as the number of equivalents of a particular ion per equivalent of resin.

Results

A plot of the total volume of the eluate versus the positions of the boundaries between the bands indicated that the neodymium band was essentially constant in length after a short initial adjustment and that the band moved at a constant rate with respect to the total volume of the eluate. The length of the copper-ammonium-hydrogen band was constant within experimental error for runs 27 and 28. However, the length of the copper-ammonium-hydrogen band in run 29 continued to increase at a continually increasing rate until after the neodymium had moved approximately one band length. Thereafter, the length of the band continued to increase at a constant rate.

The concentrations of the various species such as ammonium, neodymium, copper, and hydrogen in the eluate samples were essentially constant for the individual bands except for the copper-ammonium-hydrogen band in elution 29. The first two-thirds of this band was constant in composition. However, in the last third of the copper-ammonium-hydrogen band, the copper concentration slowly decreased and the ammonium concentration slowly increased until the neodymium band appeared. This non-uniform region will be discussed later in the Discussion of Results. The two appendages taken from the copper-ammonium-hydrogen band had almost exactly the same composition since they were taken from the region of the band in which the concentration of the species in solution are constant.

The two appendages taken from the neodymium band in run 29 had essentially the same composition; and, likewise, this was true for runs 27 and 28.

A precipitate appeared in each of the eluate samples from the neodymium band in elution 29 after standing for a day. A recorded amount of ammonia had to be added to each of the solutions in order to cause the precipitate to dissolve. After the solutions were analyzed, the results were corrected for the extra ammonia added and the dilution of the eluate samples. This phenomenon will also be discussed later.

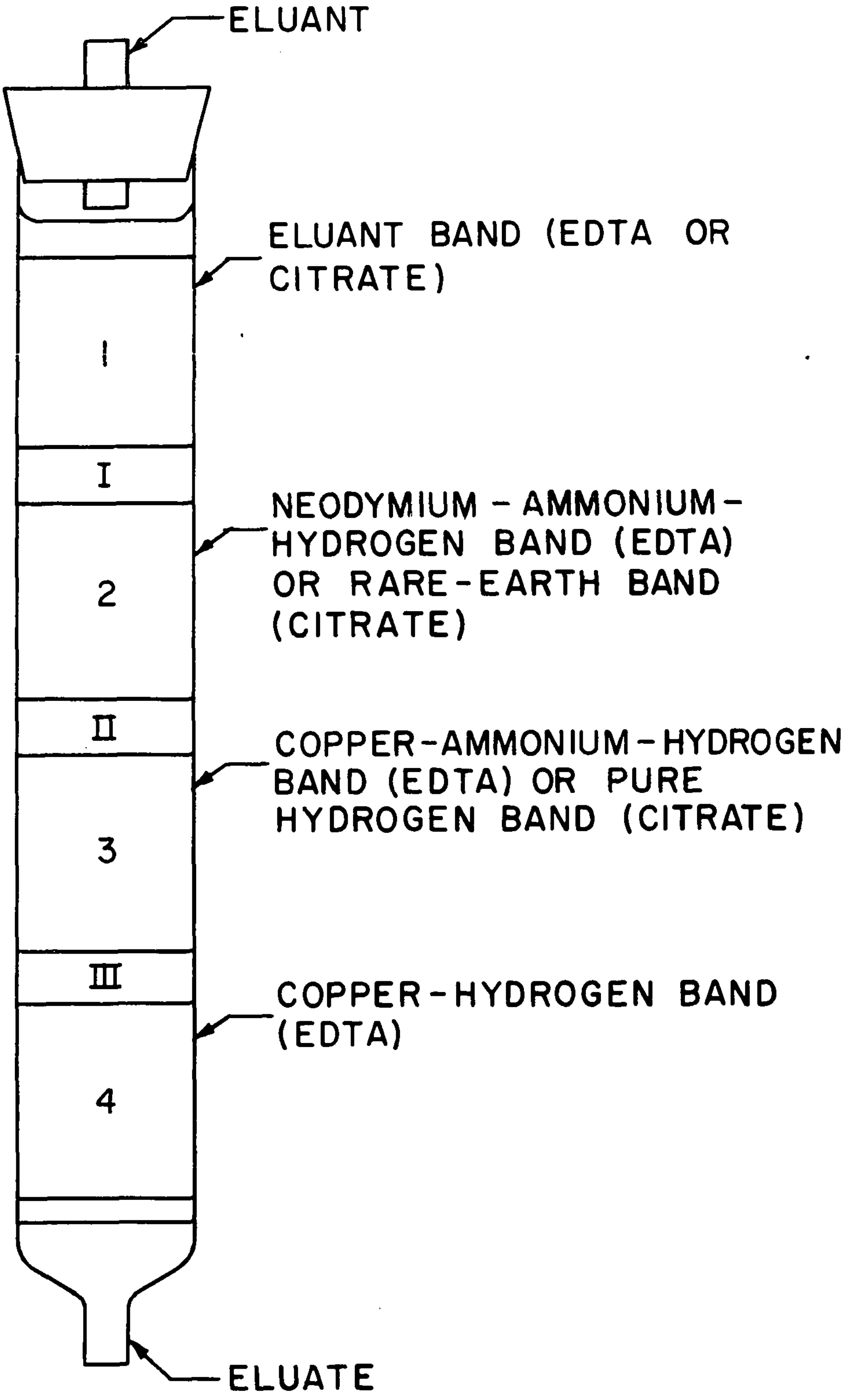
The results of these three runs are recorded in Table 1.

THEORETICAL DISCUSSION

In the elution system studied previously by Spedding, Powell, and co-workers (56, 57), an ammonia-buffered citrate solution was used as the eluant, and a hydrogen-form resin was used as a retaining bed for the rare earths. The elution system has three equilibrium elution bands which are in equilibrium with (1) the eluant, (2) the rare-earth eluate, and (3) the pure citric acid. The boundary regions between these bands will be designated as regions I and II.

The elution system studied in this thesis is labeled as shown in Figure 6. The "flat" equilibrium type regions are (1) the ammonium band in equilibrium with the eluant, (2) the neodymium-ammonium-hydrogen band in equilibrium with the eluate, (3) the copper-ammonium-hydrogen band in equilibrium with its eluate, and (4) the predetermined copper-hydrogen retaining bed in equilibrium with its eluate issuing from the column. In these equilibrium bands which give the "flat" type equilibrium curves, the concentration of all of the ions and molecules will remain constant in the eluate which is in contact with a particular band. Also, the concentration of the ions on the resin in terms of equivalent fraction will remain the same from top to bottom. The solution and resin phases will be in equilibrium and no net transfer of any ionic species will occur between the two phases. The short regions between the four equilibrium bands are the boundary regions

Figure 6. Schematic drawing of the equilibrium bands and the boundary regions between these bands for elutions with an ammonia-buffered EDTA eluant or with an ammonia-buffered citric acid eluant


ELUANT
ELUANT BAND (EDTA OR CITRATE)
1
I
NEODYMIUM - AMMONIUM-HYDROGEN BAND (EDTA) OR RARE-EARTH BAND (CITRATE)
2
II
COPPER-AMMONIUM-HYDROGEN BAND (EDTA) OR PURE HYDROGEN BAND (CITRATE)
3
III
COPPER-HYDROGEN BAND (EDTA)
4
ELUATE

I, II, and III. These short regions occur because various reactions go to completion in a very small distance within an elution column, and a particular atomic species will be completely adsorbed by the resin or completely removed from the resin in this short region on the column.

For these conditions, all net transfers between the two phases will occur only in the boundary regions. The rate at which these transfers take place depends on the eluant flow rate, the chemical constraints set up in the boundary regions, and the rate of the chemical reactions. That is, the boundary regions will be short if the chemical reactions in these regions have large equilibrium constants and the reactions take place rapidly. Since the solution phase is flowing past the resin phase, the two phases may not quite reach equilibrium in the boundary because the solution is flowing away from the resin where the solution was tending to approach equilibrium. However, if a constant flow rate is maintained, the boundary regions will attain a steady state and a continuous gradient will occur in both phases.

In the equilibrium bands, the equilibria attained and the length of the band will depend on the particular ions present, the complexes formed in solution, the resin used, and the net transport across the boundary regions from one equilibrium band to the next. If an atomic species is transported out of one boundary at the same rate that it is transported into the other boundary, the equilibrium band will remain a constant length.

On the other hand, if there is a net transport of one or more atomic species through the upper boundary which differs from the net transport through the lower boundary, then the band will either grow or shrink. If this band is to show an equilibrium type behavior, then the transport of the atomic species into the band at the upper boundary must be compensated by the leak through of other atomic species at the lower boundary so that the relative composition of the band will remain unchanged. Then the band will grow at the same rate the total equivalents are leaking into the band. It follows that, if such equilibrium bands are to be maintained, the equilibria and net transport at the boundaries will be determined by the composition of the eluant entering the top of the column and by the composition of the final retaining bed.

The eluant which flows into the top of the column at a uniform rate is a solution of a chelating acid which is usually buffered with ammonium hydroxide to a desired pH and has a homogeneous composition. This solution drives the bands already adsorbed on the column down its length and at the same time forms a new band which rapidly comes to equilibrium with the eluant. After this equilibrium has been established, there will no longer be any net transfer between the resin and the solution phase; and the solution phase will be the same as the eluant. This portion of the column which has achieved complete equilibrium will be designated as the eluant band or region 1. The boundary region where net transfer takes place is labeled region I.

Before the two eluant bands are considered, the symbols used in the remainder of the thesis will be defined. It should be noted that when the charge of the ion or molecule is omitted from the symbol, the symbol indicates a molar concentration in solution or a concentration of an ion on the resin in terms of equivalent fraction. The term equivalent fraction indicates the number of equivalents of a particular ion per equivalent of resin on the basis that one mole of hydrogen ion, one mole of ammonium ion, one mole of cupric ion, and one mole of neodymium ion are equal to one equivalent of hydrogen ion, one equivalent of ammonium ion, two equivalents of cupric ion, and three equivalents of neodymium ion, respectively.

Cit_T = the total molar concentration of the citrate group in all of the ions and molecules in solution.

Y_T = the total molar concentration of EDTA in all of the ions and molecules of the solution.

NH_{4T} = the total molar concentration of the NH_4 groups.

H_T = the total molar concentration of the replaceable hydrogen.

h_T = the total replaceable hydrogen in the eluate (H_T) minus the total replaceable hydrogen in the eluant ($\bar{H}_T$).

Cu_T = the total molar concentration of copper.

R_T = the total molar concentration of a rare earth.

Nd_T = the total molar concentration of neodymium.

Cit = molar concentration of the trinegative citrate ion, Cit^{-3}.

HCit = molar concentration of $HCit^{-2}$.

H_2Cit = molar concentration of H_2Cit^{-1}.

H_3Cit = molar concentration of H_3Cit^{o}.

$RCit_2$ = the molar concentration of $RCit_2^{-3}$.

$HRCit_2$ = the molar concentration of $HRCit_2^{-2}$.

RCitOH = the molar concentration of $RCitOH^{-}$.

Y = the molar concentration of the tetranegative EDTA ion, Y^{-4}.

HY = the molar concentration of HY^{-3}.

H_2Y = the molar concentration of H_2Y^{-2}.

H_3Y = the molar concentration of H_3Y^{-1}.

H_4Y = the molar concentration of H_4Y^{o}.

OH = the molar concentration of OH^{-1}.

H = the molar concentration of the hydrogen ion, H^{+}.

NH_4 = the molar concentration of the ammonium ion, NH_4^{+}.

NH_4OH = the molar concentration of NH_4OH^{o}.

Cu = the molar concentration of the cupric ion, Cu^{+2}.

CuY = the molar concentration of CuY^{-2}.

HCuY = the molar concentration of $HCuY^{-1}$.

H_2CuY = the molar concentration of H_2CuY^{o}.

Nd = the molar concentration of the neodymium ion, Nd^{+3}.

NdY = the molar concentration of NdY^{-}.

$HNdY$ = the molar concentration of $HNdY^{o}$.

E_{NH_4} = the equivalent fraction of NH_4^{+} on the resin.

E_H = the equivalent fraction of H^{+} on the resin.

E_{Cu} = the equivalent fraction of Cu^{+2} on the resin.

E_{Nd} = the equivalent fraction of Nd^{+3} on the resin.

E_R = the equivalent fraction of R^{+3} on the resin.

A bar is used over these symbols to indicate the species or their concentrations in the eluant. For example, $\overline{NH}_{4T}$, $\overline{Cit}$, $\overline{Y}_T$, and $\overline{H}_T$ express the concentrations in the eluant. The ammonia-buffered citric acid solution and the ammonia-buffered EDTA solution are the two eluants used.

Ammonia-Buffered-Citric-Acid Eluant Band

The eluant is a citric acid solution of known concentration buffered with NH_4OH to the desired pH, usually in the region of 5 to 7. Electroneutrality of the eluant requires that the sum of the positive charges should equal the sum of the negative charges; thus,

$$\overline{NH}_{4T} + \overline{H}_T = 3\ \overline{Cit}_T \ . \qquad (3)$$

Since $\overline{NH}_{4T}$ and $\overline{Cit}_T$ are determined experimentally, this equation establishes $\overline{H}_T$.

The high pH of the eluant causes some hydrolysis of the ammonium ion; therefore,

$$\overline{NH}_{4T} = \overline{NH}_4 + \overline{NH}_4\overline{OH} \ . \qquad (4)$$

Due to the hydrolysis,

$$\overline{NH_4^+} + \overline{H_2O}^{0} \rightleftharpoons \overline{NH_4OH}^{0} + H^+ \;, \tag{5}$$

and
$$K'_K = \frac{\overline{NH_4OH} \times \overline{H}}{\overline{NH_4}} \;. \tag{6}$$

Thus,
$$\overline{NH_4OH} = K'_K \, \frac{\overline{NH_4}}{\overline{H}} \;, \tag{7}$$

and
$$\overline{NH_4}_T = \overline{NH_4} + K'_K \, \frac{\overline{NH_4}}{\overline{H}} . \tag{8}$$

The following reactions occur in solution and attain equilibrium:

$$\overline{H}^+ + \overline{Cit}^{-3} \rightleftharpoons \overline{HCit}^{-2} \;, \tag{9}$$

and
$$K'_3 = \frac{\overline{HCit}}{\overline{H} \times \overline{Cit}} \;, \tag{10}$$

or
$$\overline{HCit} = K'_3 \, \overline{H} \times \overline{Cit} \;; \tag{11}$$

$$\overline{H}^+ + \overline{HCit}^{-2} \rightleftharpoons \overline{H_2Cit}^- \;, \tag{12}$$

and
$$K'_2 = \frac{\overline{H_2Cit}}{\overline{H} \times \overline{HCit}} \;, \tag{13}$$

or
$$\overline{H_2Cit} = K'_2 K'_3 \, \overline{H}^2 \times \overline{Cit} \;; \tag{14}$$

$$\overline{H}^+ + \overline{H_2Cit}^- \rightleftharpoons \overline{H_3Cit}^{0} \;, \tag{15}$$

and
$$K_1 = \frac{\overline{H_3Cit}}{\overline{H} \times \overline{H_2Cit}} \;, \tag{16}$$

or
$$\overline{H_3Cit} = K'_1 K'_2 K'_3 \, \overline{H}^3 \times \overline{Cit} \;. \tag{17}$$

The concentration of any complex ion in the solution may be expressed as the product of the apparent equilibrium constant and the concentrations of the simple ions such as H^+, Cit^{-3}, and NH_4^+.

Since the apparent equilibrium constants (K_1', K_2', K_3', etc.) are products and ratios of concentrations rather than activities, they will vary slightly with ionic strength. These apparent constants may be determined experimentally for the desired conditions. Although it is less desirable, these constants also may be calculated from thermodynamic constants or apparent constants at another ionic strength using the Deybe-Hückel theory (70).

Since the solution phase in contact with the eluant-band resin has the same composition as the eluant, the material balance equations may be defined as follows:

$$\overline{Cit}_T = \overline{Cit} + \overline{HCit} + \overline{H_2Cit} + \overline{H_3Cit} \ , \qquad (18)$$

or

$$\overline{Cit}_T = (1 + K_3'\overline{H} + K_2'K_3'\overline{H}^2 + K_1'K_2'K_3'\overline{H}^3)\ \overline{Cit} \ ; \qquad (19)$$

and

$$\overline{H}_T = 3\overline{H_3Cit} + 2\overline{H_2Cit} + \overline{HCit} + \overline{H} - \overline{NH_4OH} \ , \qquad (20)$$

or

$$\overline{H}_T = (3K_1'K_2'K_3'\overline{H}^3 + 2K_2'K_3'\overline{H}^2 + K_3'\overline{H})\overline{Cit} + \overline{H} - K_X' \frac{\overline{NH_4}}{\overline{H}} \ . \qquad (21)$$

The three equations 8, 19, and 21 establish the values of the three unknowns $\overline{H}$, $\overline{NH_4}$, and $\overline{Cit}$. Then the concentration of each of the complex species may be calculated from the values of these simple ions. Thus, the composition of the eluant is completely established by $\overline{NH_4}_T$, $\overline{Cit}_T$, and the apparent equilibrium constants.

The equilibrium between the eluant and the resin in region 1 may be expressed as follows where $\overline{NH}^+_{4_r}$ and $\overline{H}^+_r$ represent the ammonium and hydrogen ions on the resin:

$$\overline{H}^+_r + \overline{NH}^+_4 \rightleftharpoons \overline{H}^+ + \overline{NH}^+_{4_r} , \tag{22}$$

and

$$K'_F = \frac{\overline{H} \times \overline{E}_{NH_4}}{\overline{NH}_4 \times \overline{E}_H} . \tag{23}$$

The K'_F is approximately equal to one, $\overline{H}$ to 10^{-6} moles per liter, and $\overline{NH}_4$ to 10^{-2} moles per liter. Thus the ratio of $\overline{E}_H$ to $\overline{E}_{NH_4}$ is equal to approximately 10^{-4} and the equivalent fraction of ammonium on the resin, $\overline{E}_{NH_4}$, may be set equal to 1.000. Therefore, the only ion that may be transferred to the resin in the lower boundary region I of the eluant band is the ammonium ion since almost all of the hydrogen and all of the other ions will be removed from the resin in region 1.

Let N_I equal the equivalents of resin that the boundary region I traverses as one liter of eluant passes into the top of the column. Since the resin is packed uniformly in a column, the amount of eluate surrounding one equivalent of resin (f), irrespective of the ions adsorbed, is the same when the difference in swelling is neglected.

Since fN_I liters of eluant are required to surround the N_I equivalents of resin which develop in the eluant band, only 1 - fN_I liters of eluant move into boundary I. Thus, let

$$V_I = 1 - fN_I$$

where V_I is the volume of eluant entering boundary I.

Since almost none of the replaceable hydrogen in the eluant may be laid down on the resin to drive the other bands ahead of the eluant band, only the ammonium ions which are laid down in the boundary region forming ammonium resin cause the boundary to move. Therefore,

$$N_I = \overline{NH}_{4_T}V_I - T^I_{NH_4} = \overline{NH}_{4_T}(1 - fN_I) - T^I_{NH_4} \; . \qquad (24)$$

The $T^I_{NH_4}$ represents the net equivalents of ammonium which leak through boundary I into region 2 as one liter of eluant flows in the top of the column. When there is a net transport of ammonium from region 2 into region 1, arising from ammonium ion on the resin in region 2 leaking through the boundary into region 1, $T^I_{NH_4}$ takes on a negative value and the boundary moves faster than is indicated by $\overline{NH}_4(1 - fN_I)$. When no leak through occurs, the boundary moves at the $\overline{NH}_{4_T}V_I$ rate.

Ammonia-Buffered-EDTA Eluant Band

In this case the eluant is made up to a known concentration of ethylenediaminetetraacetic acid and is buffered to the desired pH, usually in the 8 to 9 range.

The equilibria and the mass transport in this eluant band are very similar to the citrate-eluant band. The same type of equations apply; therefore,

$$\overline{H}_T + \overline{NH}_{4_T} = 4\overline{Y}_T \qquad (25)$$

and $$\overline{NH_4}_T = \overline{NH_4} + \overline{NH_4OH} = \overline{NH_4} + K'_K \frac{\overline{NH_4}}{\overline{H}} \ . \qquad (26)$$

The following reactions occur and attain equilibrium:

$$\overline{H}^+ + \overline{Y}^{-4} \rightleftharpoons \overline{HY}^{-3} \ , \qquad (27)$$

and $$K'_4 = \frac{\overline{HY}}{\overline{H} \times \overline{Y}} \ , \qquad (28)$$

or $$\overline{HY} = K'_4\overline{H} \times \overline{Y} \ ; \qquad (29)$$

$$\overline{H}^+ + \overline{HY}^{-3} \rightleftharpoons \overline{H_2Y}^{-2} \ , \qquad (30)$$

and $$K'_3 = \frac{\overline{H_2Y}}{\overline{H} \times \overline{Y}} \ , \qquad (31)$$

or $$\overline{H_2Y} = K'_3K'_4\overline{H}^2 \times \overline{Y} \ ; \qquad (32)$$

$$\overline{H}^+ + \overline{H_2Y}^{-2} \rightleftharpoons \overline{H_3Y}^- \ ; \qquad (33)$$

and $$K'_2 = \frac{\overline{H_3Y}}{\overline{H} \times \overline{H_2Y}} \ , \qquad (34)$$

or $$\overline{H_3Y} = K'_2K'_3K'_4\overline{H}^3 \times \overline{Y} \ ; \qquad (35)$$

$$\overline{H}^+ + \overline{H_3Y}^- \rightleftharpoons \overline{H_4Y}^0 \ , \qquad (36)$$

and $$K'_1 = \frac{\overline{H_4Y}}{\overline{H} \times \overline{H_3Y}} \ , \qquad (37)$$

or $$\overline{H_4Y} = K'_1K'_2K'_3K'_4\overline{H}^4 \times \overline{Y} \ . \qquad (38)$$

Since the whole must be equal to the sum of the parts for both the total EDTA and the total replaceable hydrogen of the eluant, the following material balance equations apply:

$$\bar{Y}_T = \bar{Y} + \overline{HY} + \overline{H_2Y} + \overline{H_3Y} + \overline{H_4Y} \ , \qquad (39)$$

or $$\bar{Y}_T = (1 + K_4'\bar{H} + K_3'K_4'\bar{H}^2 + K_2'K_3'K_4'\bar{H}^3 + K_1'K_2'K_3'K_4'\bar{H}^4)\bar{Y} \ . \qquad (40)$$

$$\bar{H}_T = \overline{HY} + 2\overline{H_2Y} + 3\overline{H_3Y} + 4\overline{H_4Y} + \bar{H} - \overline{NH_4OH} \ , \qquad (41)$$

or $$\bar{H}_T = K_4\bar{H} + 2K_3'K_4'\bar{H}^2 + 3K_2'K_3'K_4'H^3 + 4K_1'K_2'K_3'K_4'\bar{H}^4$$
$$+ \bar{H} - K_K' \frac{\overline{NH_4}}{\bar{H}} \ . \qquad (42)$$

As in the previous eluant band which developed by using an ammonia-buffered-citrate solution, the concentration of the three simple ions ($\bar{H}$, $\overline{NH_4}$, and $\bar{Y}$) are established by the three equations 26, 40, and 42. The concentration of each of the complex species may be calculated from the values of these three simple ions. Therefore, the composition of the eluant is completely established by $\overline{NH_4}_T$ and $\bar{Y}_T$.

Again, the same arguments apply for the lower boundary of the eluant band, because only ammonium ion may be laid down on the resin in the boundary region; therefore,

$$N_I = (4\bar{Y}_T - \bar{H}_T)V_I - T^I_{NH_4} = \overline{NH_4}V_I - T^I_{NH_4} \ . \qquad (43)$$

The symbol N_I is again the number of resin equivalents which the eluant band increases in length or the rate the boundary moves per liter of eluant entering the column. The V_I is the volume of the eluant flowing into boundary I or the liters of eluate flowing out of this boundary, and $T^I_{NH_4}$ is the net equivalents of ammonium transported down through this boundary as a liter of eluant passes in through the top of the column. The volume of the eluant required to surround the resin in the developing eluant band, fN_I, does not pass into the boundary region. Thus,

$$V_I = 1 - fN_I \; . \tag{44}$$

The fact that the resin is driven to equilibrium with the eluant within the eluant band puts a constraint on this system, i.e., the total replaceable hydrogen, $\bar{H}_T$, must be transported intact through boundary I in the solution phase. Since the ammonium is compatable with both the solution and the resin phases in the eluant band, it may be transported into the eluant band on the resin or out of the band in the solution. It will be shown that the rate at which the ammonium is transported through this boundary, $T^{I}_{NH_4}$, is determined by constraints imposed by the top boundary region of the final retaining resin bed.

Pure Hydrogen Resin as a Final Retaining Bed

A retaining bed is chosen so that the chemical reactions which occur within its upper boundary cause all of the ions which are not compatible with this bed to be transferred to the resin. At the same time, an equivalent amount of ions compatible with the retaining bed enter the eluate. If the proper homogeneous retaining bed has been chosen, the composition of the eluate will be so adjusted that it is in equilibrium with the retaining bed and no further net transfer occurs between the solution and the resin phases. A pure hydrogen bed has been used successfully with the ammonia-buffered citric-acid eluant and a homogeneous copper-hydrogen bed with the ammonia-buffered EDTA eluant.

The eluate in equilibrium with the pure hydrogen bed is a pure citric acid solution; so

$$H_T^* = 3Cit_T^* , \qquad (45)$$

and

$$E_H^* = 1 . \qquad (46)$$

The asterisk (*) will be used to designate quantities associated with the final retaining bed.

Since species containing citrate groups are not absorbed anywhere along the column, the total citrate concentration will not change as the eluate passes over various sections of the resin; thus,

$$\overline{Cit}_T = Cit_T^* = (1 + K_3'H^* + K_2'K_3'H^{*2} + K_1'K_2'K_3'H^{*3})Cit^* , \qquad (47)$$

and

$$3\overline{Cit}_T = 3Cit_T^* = H_T^* = (3K'K_1'K_2'H_3^{*3} + 2K_2'K_3'H^{*2} + K_3'H^*)Cit^* + H^*. \qquad (48)$$

These two equations determine the values of Cit^* and H^* and, therefore, the concentration of each of the complex species. Thus, conditions in this region are determined by $E_H^* = 1$, the value of $\overline{Cit}_T$, and apparent equilibrium constants.

In the boundary region II, immediately above region 3 (the pure hydrogen band), all of the ammonium ion and all other cations, except hydrogen, must be deposited on the resin. It was shown that all of the replaceable hydrogen in the eluant must be transported through the boundary region I which is below region 1. If the region 3 is immediately below the eluant band, then boundary region I is identically the same as boundary region II.

The following reactions then occur at this boundary:

$$H_r^+ + NH_4^+ + Cit^{-3} \rightleftharpoons NH_{4r}^+ + HCit^{-2} , \qquad (49)$$

$$H_r^+ + NH_4^+ + HCit^{-2} \rightleftharpoons NH_{4r}^+ + H_2Cit^- , \qquad (50)$$

and

$$H_r^+ + NH_4^+ + H_2Cit^- \rightleftharpoons NH_{4r}^+ + H_3Cit^0 . \qquad (51)$$

All of these reactions are rapid and have large equilibrium constants. Therefore, these reactions go to completion within a very short distance on the column and the boundary region is very narrow.

The total replaceable hydrogen in one liter of the eluate (H_T^*) flowing out of the boundary comes from two sources. The first is the hydrogen ion being transferred from the resin to the eluate in the boundary ($E_H^* - \bar{E}_H$) and the second is the total replaceable hydrogen in the eluant which is being transported through the boundary in the solution phase. Thus,

$$H_T^* V_{II} = N_{II}(E_H^* - \bar{E}_H) + \bar{H}_T V_{II} . \qquad (52)$$

The symbol N_{II} represents the equivalents of resin which the boundary II moves, and V_{II} represents the liters of eluant flowing into boundary II as one liter of eluant flows in the top of the column. The symbol $\bar{E}_H$ indicates the quantity of hydrogen which remains on the resin to be transported up through the boundary. However, it has been shown that $\bar{E}_H$ is extremely small. Thus,

$$N_{II} = N_I = (H_T^* - \bar{H}_T)(1 - fN_{II}) = \overline{NH}_4(1 - fN_I) - T^I_{NH_4} . \quad (53)$$

Since boundaries I and II are identical and no ammonium enters region 3, $T^I_{NH_4}$ must equal zero.

Rare-Earth Equilibrium Band

If a rare-earth band is inserted between the boundary regions I and II, a number of reactions of the following type will occur in boundary I:

$$R_r^{+3} + 2Cit^{-3} + 3NH_4^+ \rightleftharpoons 3NH_{4_r}^+ + RCit_2^{-3} , \quad (54)$$

$$H^+ + RCit_2^{-3} \rightleftharpoons HRCit_2^{-2} , \quad (55)$$

and

$$RCit_2^{-3} + H_2O^0 \rightleftharpoons RCitOH^- + H^+ + Cit^{-3} . \quad (56)$$

All of the rare-earth citrate complexes have very large stability constants so all of the rare earth on the resin is picked up in a very short distance along the column. Since the eluant has a high pH, the relative Cit^{-3} concentration is large. However, as the rare-earth citrate complexes are formed in the eluate, hydrogen ion is liberated so that a marked lowering of the pH occurs in this region. If the initial rare-earth band inserted between the boundaries is too concentrated in rare-earth ion, the eluate and the resin bed will be out of equilibrium. Some ammonium ions will leak through boundary I making the eluate too high in ammonium. This ammonium will start to exchange with the rare-earth resin and the band will grow since all of the ammonium and rare-earth are deposited at boundary II.

While ammonium and hydrogen ions are being transported into region 2, the top boundary moves more slowly than the equilibrium band. The rare-earth band will lengthen as ammonium and hydrogen dilute the fixed amount of rare earth in the band. The lower boundary will travel at almost the equilibrium rate because all of the ammonium is transferred to the resin at this point. The very small amount of hydrogen which is transported into the band through the lower boundary as it lengthens causes the band initially to move at a slightly faster rate.

Ultimately, a mixed rare-earth-ammonium-hydrogen bed of fixed composition will come to equilibrium with the eluate and the band will move down the column with constant length. The same number of equivalents of rare earth, ammonium, and hydrogen picked up by the eluate in region I will be redeposited in region II. When the eluate encounters the hydrogen retaining bed in region II, the pH is again markedly lowered so that the ionic species in the eluate are mainly H_3Cit and H_2Cit^-.

These complexes have much larger stability constants than the rare-earth citrate complexes so that in a very short distance along the column the rare earth is redeposited liberating hydrogen ions from the resin. Also, the ammonium ions will exchange with hydrogen ions since the hydrogen citrate species have high stability constants and this results in ammonium being deposited simultaneously with the rare earth. As a result of these reactions, all of the ammonium ions and the rare-earth ions are deposited on the resin in region II and the eluate flowing over the hydrogen retaining bed becomes pure citric acid. Since the two boundaries move at the same rate under equilibrium conditions,

$$N_I = N_{II} = \overline{NH}_{4_T} V_I = (3\overline{Cit} - \overline{H}_T) V_{II} \, , \qquad (57)$$

and

$$V_I = V_{II} = (1 - fN_I) \; ; \qquad (58)$$

therefore,

$$N_I = \frac{\overline{NH}_{4_T}}{1 + f\overline{NH}_{4_T}} \, . \qquad (59)$$

Since there is no net transport of ammonium through either boundary and the $\overline{H}_T$ is transported through each boundary, N_I equivalents of ammonium in the eluant may be considered completely laid down in boundary I and all of the N_I equivalents of cations in the rare-earth band may be considered completely transferred into the V_I liters of eluate. Then,

$$3R_T V_I = N_I E_R \, , \qquad (60)$$

$$NH_4V_I = N_IE_{NH_4} , \qquad (61)$$

and

$$(H_T - \overline{H}_T)V_I = N_IE_H \qquad (62)$$

where

$$\frac{V_I}{N_I} = \frac{V_I}{V_I\overline{NH}_{4_T}} = \frac{1}{\overline{NH}_{4_T}} . \qquad (63)$$

Thus,

$$E_R = 3R_T \frac{V_I}{N_I} = \frac{3R_T}{\overline{NH}_{4_T}} , \qquad (64)$$

$$E_{NH_4} = \frac{NH_4}{\overline{NH}_{4_T}} , \qquad (65)$$

and

$$E_H = \frac{H_T - \overline{H}_T}{\overline{NH}_{4_T}}. \qquad (66)$$

The following equations may be written for the equilibria between the solution and resin phases:

$$NH_4^+ + H_r^+ \rightleftharpoons H^+ + NH_{4r}^+ , \qquad (67)$$

and

$$K_F' = \frac{H \times E_{NH_4}}{NH_4 \times E_H} , \qquad (68)$$

$$R^{+3} + 3NH_{4r}^+ \rightleftharpoons 3NH_4^+ + R_r^{+3} , \qquad (69)$$

and

$$K_I' = \frac{(NH_4)^3 \times E_R}{R \times (E_{NH_4})^3} . \qquad (70)$$

The third expression may be derived from the other two equations and is not independent; that is,

$$R^{+3} + 3H_r^+ \rightleftharpoons 3H^+ + R_r^{+3} , \qquad (71)$$

and $$K_J' = \frac{(H)^3 \times E_R}{R \times (E_H)^3} = K_I'(K_F')^2 \ . \qquad (72)$$

Substituting the values for E_R, E_{NH_4}, and E_H obtained from equations 64, 65, and 66 into equations 68 and 70, gives the following equations:

$$K_F' = \frac{H}{H_T - \overline{H}_T} \ ; \qquad (73)$$

thus, $$H_T = \overline{H}_T + \frac{H}{K_F'} \ ; \qquad (74)$$

and $$K_I' = \frac{3R_T(\overline{NH}_{4_T})^2}{R} \ ; \qquad (75)$$

thus, $$R_T = \frac{K_I'R}{3(\overline{NH}_{4_T})^2} \ . \qquad (76)$$

The reactions which attain equilibrium in the eluate of the rare-earth band are the following:

$$R^{+3} + 2Cit^{-3} \rightleftharpoons RCit_2^{-3} \ , \qquad (77)$$

and $$K_5' = \frac{RCit_2}{R \times (Cit)^2} \ , \qquad (78)$$

or $$RCit_2 = K_5'R(Cit)^2 \ ; \qquad (79)$$

$$H^+ + RCit_2^{-3} \rightleftharpoons HRCit_2^{-2} \ , \qquad (80)$$

and $$K_6' = \frac{HRCit_2}{H \times RCit_2} \ , \qquad (81)$$

or $$HRCit_2 = K_6'K_5'H \times R(Cit)^2 \ ; \qquad (82)$$

$$H_2O^o + RCit_2^{-3} \rightleftharpoons RCitOH^{-2} + Cit^{-3} + H^+ \qquad (83)$$

and

$$K_7' = \frac{RCitOH \times Cit \times H}{RCit_2} \qquad (84)$$

or

$$RCitOH = K_7'K_5' \frac{R \times Cit}{H} . \qquad (85)$$

The following reactions have been discussed previously on page 50 in this thesis:

$$H_iCit^{-(3-i)} + H^+ \rightleftharpoons H_{i+1}Cit^{-(2-i)} \quad (i = 0,1,2). \qquad (86)$$

The material balance equations for H_T and R_T may be written as follows:

$$H_T = H + 3H_3Cit + 2H_2Cit + HCit - RCitOH + HRCit_2 \; ; \qquad (87)$$

therefore,

$$\overline{H}_T + \frac{H}{K_F'} = H + (3K_1'K_2'K_3'H^3 + 2K_2'K_3'H^2 + K_3H - K_7'K_5' \frac{R}{H}$$
$$+ K_6'K_5'H \times R \times Cit)Cit . \qquad (88)$$

$$R_T = R + RCit_2 + HRCit_2 + RCitOH \; ; \qquad (89)$$

therefore,

$$\frac{K_I'R}{3(\overline{NH}_{4_T})^2} = R + K_5'R \times (Cit)^2 + K_6'K_5'H \times R \times (Cit)^2 + K_7'K_5'\frac{R \times Cit}{H}$$
$$(90)$$

or

$$\frac{K_I'}{3(NH_{4_T})^2} = 1 + K_5'(Cit)^2 + K_6'K_5'H \times (Cit)^2 \times K_7'K_5' \frac{Cit}{H} .$$
$$(91)$$

Since no ion or molecule containing a citrate group is adsorbed by the resin anywhere along the column, the following material balance equation may be written for Cit_T:

$$\overline{Cit_T} = Cit_T = Cit + HCit + H_2Cit + H_3Cit + 2RCit_2 + 2HRCit_2 + RCitOH \; ; \qquad (92)$$

therefore,

$$\overline{Cit} = (1 + K_3'H + K_2'K_3'H^2 + K_1'K_2'K_3'H^3 + 2K_5'R \times Cit + 2K_6'K_5'H \times R \times Cit + K_7'K_5' \tfrac{R}{H})Cit \; . \qquad (93)$$

The charge balance in solution requires that the following equation be valid:

$$NH_4 + H + 3R = 3Cit + 2HCit + H_2Cit + 3RCit_2 + 2HRCit_2 + RCitOH \; ; \qquad (94)$$

therefore,

$$NH_4 + H + 3R = (3 + 2K_3'H + K_2'K_3'H^2 + 3K_5'R \times Cit + 2K_6'K_5'H \times R \times Cit + K_7'K_5' \tfrac{R}{H})Cit \; . \qquad (95)$$

Since the three equations 88, 91, and 93 have only the three unknowns H, R, and Cit, these unknowns may be determined by solving these three equations simultaneously. The values of H_T, R_T, NH_4, E_H, E_R, and E_{NH_4} are determined by the equations 74, 76, 95, 66, 64, and 65, respectively, and the values of H, R, and Cit. The concentration of the complexes also are determined by the values of H, R, and Cit.

Homogeneous Copper-Hydrogen as Final Retaining Bed

The resin bed in region 4 is a homogeneous copper-hydrogen resin. If an equilibrium band is to be established, the eluate will have to come to equilibrium with the resin phase.

Thus, the eluate will contain only H^+ and Cu^{+2} ions and complexes of these ions with the EDTA.

Retaining bed with no transport

When the copper-hydrogen bed is placed directly below this eluant band, the following reactions occur at the boundary between these two bands:

$$2NH_4^+ + Cu_r^{+2} + Y^{-4} \rightleftharpoons 2NH_{4r}^+ + CuY^{-2} \qquad (96)$$

$$2NH_4^+ + Cu_r^{+2} + HY^{-4} \rightleftharpoons 2NH_{4r}^+ + HCuY^- \qquad (97)$$

$$NH_4^+ + H_r^+ + CuY^{-2} \rightleftharpoons NH_{4r} + HCuY^- \qquad (98)$$

$$NH_4^+ + H_r^+ + HCuY^- \rightleftharpoons NH_{4r} + H_2CuY^0 \qquad (99)$$

These reactions have large apparent equilibrium constants and cause the copper and hydrogen ions on the resin to be removed within a very short distance on the column. However, for each eluant of a fixed composition there is only one composition of the copper-hydrogen resin which is compatible with that eluant such that no net transports occur at the boundary except the $\overline{H}_T$ and $\overline{Y}_T$ of the eluant which pass through all boundaries unchanged.

Since all of the ammonium is transferred to the resin in boundary III, the boundary will move N_{III} equivalents, where

$$\overline{NH}_{4_T} V_{III} = N_{III} \overline{E}_{NH_4} = N_{III} \;, \qquad (100)$$

and

$$\frac{V_{III}}{N_{III}} = \frac{1}{\overline{NH}_{4_T}} \;. \qquad (101)$$

The symbol N_{III} refers to the number of equivalents of resin over which boundary III moves and symbol V_{III} to the liters of eluate which flow through this boundary as exactly one liter of eluant flows into the top of the column.

The copper and hydrogen are being completely transferred to the eluate at the same time as the ammonium is being completely transferred to the resin. Thus,

$$N_{III}E^{*}_{Cu} = 2Cu^{*}_{T}\,V_{III}\ , \tag{102}$$

and

$$N_{III}E^{*}_{H} = (H^{*}_{T} - \overline{H}_{T})V_{III}\ . \tag{103}$$

When N_{III} and V_{III} are eliminated from equations 102 and 103 by means of equation 101, the following equations are obtained:

$$E^{*}_{Cu} = \frac{2Cu^{*}_{T}}{\overline{NH}_{4_T}}\ , \tag{104}$$

and

$$E^{*}_{H} = \frac{h^{*}_{T}}{\overline{NH}_{4_T}} \tag{105}$$

where

$$h^{*}_{T} = H^{*}_{T} - \overline{H}_{T}\ . \tag{106}$$

The asterisk (*) indicates a species or its concentration in the copper-hydrogen retaining bed.

In the equilibrium region 4 where there is no net transfer of species between the resin and solution phases, the following reaction has achieved equilibrium:

$$Cu^{*+2} + 2H_{r}^{*+} \rightleftharpoons 2H^{*+} + Cu_{r}^{*+2}\ , \tag{107}$$

and
$$K'_E = \frac{(H^*)^2 \text{ x } E^*_{Cu}}{Cu^* \text{ x } (E^*_H)^2} \ . \tag{108}$$

Since
$$1 = E^*_{Cu} + E^*_H = \frac{h^*_T}{\overline{NH}_{4_T}} + \frac{2Cu^*_T}{\overline{NH}_{4_T}} \ , \tag{109}$$

then
$$h^*_T = \overline{NH}_{4_T} - 2Cu^*_T \tag{110}$$

and
$$K'_E = \frac{(H^*)^2(2Cu^*_T)\overline{NH}_4}{Cu^*(\overline{NH}_{4_T} - 2Cu^*_T)^2} \ ; \tag{111}$$

thus,
$$(Cu^*_T)^2 - \left(\overline{NH}_{4_T} + \frac{(H^*)^2\overline{NH}_{4_T}}{2K'_E Cu^*}\right)Cu^*_T + \frac{\overline{NH}^2_{4_T}}{4} = 0 \ . \tag{112}$$

Therefore, Cu^*_T may be solved as a function of the variables Cu^* and H^* by means of the quadratic formula; that is,

$$Cu^*_T = g_1(H^*, Cu^*) \ . \tag{113}$$

The reactions which attain equilibrium in the eluate are the following:

$$Cu^{*+2} + Y^{*-4} \rightleftharpoons CuY^{*-2} \ , \tag{114}$$

and
$$K'_A = \frac{CuY^*}{Cu^* \text{ x } Y^*} \ , \tag{115}$$

or
$$CuY^* = K'_A Cu^* \text{ x } Y^* \ ; \tag{116}$$

$$H^{*+} + CuY^{*-2} \rightleftharpoons HCuY^{*-} \ , \tag{117}$$

and
$$K'_B = \frac{HCuY^*}{H^* \text{ x } CuY^*} \ , \tag{118}$$

or
$$HCuY^* = K'_B H^* \text{ x } CuY^* = K'_B K'_A H^* \text{ x } Cu^* \text{ x } Y^* \ ; \tag{119}$$

$$H^{*+} + HCuY^{*-} \rightleftharpoons H_2CuY^{*o} \ , \qquad (120)$$

and
$$K_C' = \frac{H_2CuY^*}{H^* \times HCuY^*} \ , \qquad (121)$$

or
$$H_2CuY^* = K_C'K_B'H^{*2}CuY = K_C'K_B'K_A'H^{*2} \times Cu^* \times Y^* \ . \qquad (122)$$

Since very little EDTA is adsorbed anywhere along the column, Y_T^* is set equal to $\overline{Y}_T$, and the material balance equations for the copper-hydrogen band eluate may be written as follows (Y^* and HY^* may be neglected in the material balance at the low pH of this band):

$$\overline{Y}_T = Y_T^* = CuY^* + HCuY^* + H_2CuY^* + H_4Y^* + H_3Y^* + H_2Y^* \ ; \qquad (123)$$

therefore,

$$\overline{Y}_T = K_A'Cu^* \times Y^* + K_B'K_A'H^* \times Cu^* \times Y^* \times K_C'K_B'K_A'(H^*)^2 \times Cu^* \times Y^* + K_1'K_2'K_3'K_4'(H^*)^4 \times Y^* + K_2'K_3'K_4'(H^*)^3 \times Y^* + K_3'K_4'(H^*)^2 \times Y^* \ . \qquad (124)$$

$$Cu_T^* = Cu^* + CuY^* + HCuY^* + H_2CuY^* \ ; \qquad (125)$$

therefore,

$$g_1(H^*,Cu^*) = Cu^* + K_A'Cu^* \times Y^* + K_B'K_A'H^* \times Cu^* \times Y^* + K_C'K_B'K_A'(H^*)^2 \times Cu^* \times Y^* \ . \qquad (126)$$

The charge balance in the eluate may be expressed in the following manner:

$$2Cu^* + H^* = HCuY + 2CuY + H_3Y^* + 2H_2Y^* \ ; \qquad (127)$$

therefore,

$$2Cu^{*} + H^{*} = K_B'K_A'H^{*} \times Cu^{*} \times Y^{*} + K_A'Cu^{*} \times Y^{*} + K_2'K_3'K_4'(H^{*})^{3} \times Y^{*} + 2K_3'K_4'(H^{*})^{2}Y^{*}. \quad (128)$$

The three equations 124, 126, and 128 determine the three variables H^{*}, Cu^{*}, and Y^{*}. Since the concentration of each of the complexes in the eluate is determined by the values of these variables, then Cu_T^{*} is established by equation 126, h_T^{*} by equation 110, and E_{Cu}^{*} and E_H^{*} by equations 104 and 105. Therefore, there is only one composition of the resin for each eluant which will give no net transport of any of the ions except the total replaceable hydrogen and total EDTA in the eluant.

However, it is not feasible to use this retaining bed adjacent to the eluant band because the high concentration of hydrogen ion in the retaining band would precipitate H_4Y^{o} in the eluant band. Precipitation may be prevented, on the other hand, by inserting a short copper-ammonium-hydrogen band of the proper composition between the two bands without altering the boundary conditions of the eluant band or the copper-hydrogen retaining band. The copper-ammonium-hydrogen band will remain a constant length since there will be no net transports at either of the boundaries except for the $\overline{H}_T$ and $\overline{Y}_T$ which pass in through the top boundary and out through the bottom boundary. The discussion of the copper-ammonium-hydrogen band which is given later will indicate why this is true.

Retaining bed with transport

If the value of E^*_{Cu} in the homogeneous copper-hydrogen retaining bed has a value too large to be compatible with a given eluant as defined in the previous section, then E^*_H will be too small; and, conversely, if E^*_{Cu} is too small, then E^*_H is too large since

$$E^*_{Cu} + E^*_H = 1 \, . \tag{129}$$

Whatever the composition of the copper-hydrogen retaining bed, if an equilibrium band is to form, the eluate will contain only copper and hydrogen species and must come to equilibrium with the resin bed. The equilibria will be determined by the total EDTA concentration in the eluate, the composition of the resin, the values of the apparent stability constants of the complex ions formed, and the apparent equilibrium constants of the solution-resin exchange of cationic species. Since the equilibria are fixed, any adjustment in the system which will make the resin bed compatible must occur by allowing mass transport to occur through boundary region III. Therefore, a certain amount of copper or hydrogen will leak through the boundary as the band advances and, as will be shown later, will tend to form or consume a copper-ammonium-hydrogen equilibrium band.

Since the eluate comes to equilibrium with the copper-hydrogen resin, the apparent equilibrium equation

$$K'_E = \frac{(H^*)^2 \times E^*_{Cu}}{Cu^* \times (E^*_H)^2}\ , \tag{130}$$

is valid. Also, the equilibrium equations, material balance equation 124, and the charge balance equation 128, as given in the previous section, apply when the appropriate apparent constants are used. Therefore, when E^*_{Cu} and E^*_H are predetermined, this establishes the values of H^*, Cu^*, and Y^*. These ion concentrations in turn determine the concentration of all the complex ions in the eluate. The total copper (Cu^*_T) is determined by equation 124 and the total replaceable hydrogen is determined by the following equation:

$$\begin{aligned} H^*_T = 4Y^*_T - 2Cu^*_T &= H^* + K'_B K'_A H^* \times Cu^* \times Y^* + 2K'_C K'_B K'_A (H^*) \\ &\quad \times Cu^* \times Y^* + (4K'_1 K'_2 K'_3 K'_4 H^{*4} + 3K'_2 K'_3 K'_4 H^{*3} \\ &\quad + 2K'_3 K'_4 H^{*2}) Y^*\ . \end{aligned} \tag{131}$$

Therefore, the eluate composition is completely determined by the fact that $Y^*_T = \bar{Y}_T$ and the values of E^*_{Cu} and E^*_H.

When the copper-hydrogen band is not compatible with the eluant in that the copper-hydrogen ratio is too high, then the copper and hydrogen will not be completely removed at boundary III. A small quantity of the copper and hydrogen will leak through the boundary III to form a growing copper-ammonium-hydrogen band just above the boundary. Conversely, if the copper-hydrogen resin ratio is too low and a copper-ammonium-hydrogen band already exists above boundary III, then some copper and hydrogen will leak through the boundary to make up the deficiency in the copper-hydrogen band. Once the copper-ammonium-hydrogen band has vanished, then hydrogen will start accumulating in the boundary region as the band advances and will destroy the equilibrium band in region 4. If a copper-ammonium-hydrogen equilibrium band is to exist between the copper-hydrogen resin bed and the eluant band as this bed grows or shrinks, ammonium must leak through boundary II to compensate for the copper and hydrogen leak through at boundary III.

As one liter of eluant flows in through the top of the column, the boundary traverses N_{III} equivalents of resin and V_{III} liters of eluate pass down through this boundary. Also, T_{Cu}^{III} equivalents of copper and T_H^{III} equivalents of hydrogen ion are transported up through boundary III. Because the copper and hydrogen on the N_{III} equivalents of the retaining bed must either be transferred to the eluate or transported into the band above, the following equations are valid:

$$N_{III}E_{Cu}^{*} = 2Cu_T^{*}V_{III} + T_{Cu}^{III} , \qquad (132)$$

and

$$N_{III}E_H^{*} = (H_T^{*} - \overline{H}_T)V_{III} + T_H^{III} . \qquad (133)$$

Since fN_{III} liters of eluate are required to fill the N_{III} equivalents of resin phase which develop in region 3 above boundary III, only $1 - fN_{III}$ liters of eluate pass into boundary III; then,

$$V_{III} = 1 - fN_{III} \cdot$$

If this value of V_{III} is substituted into equations 132 and 133 and N_{III} is eliminated between the two equations, then the following equation is obtained:

$$T_{Cu}^{III} = \frac{(E_{Cu}^{*} + 2Cu_T^{*}f)(h_T^{*} + T_H^{III})}{E_H^{*} + h_T^{*}f} - 2Cu_T^{*} . \qquad (134)$$

The eluate concentrations h_T^{*} and Cu_T^{*} are given by equations 106, 131, and 125. Since T_{Cu}^{III} and T_H^{III} are the only unknowns in equation 134, T_{Cu}^{III} is established as a function of T_H^{III} by the constraints imposed by the retaining bed and the eluant band.

The rate at which the boundary III is driven (in equivalents of resin per liter of eluant flowing in the top of the column) is equal to the sum of the rate at which copper, ammonium, and hydrogen are laid down on the resin behind boundary III and the rate at which copper and hydrogen are transported up through boundary III via the resin. Thus,

$$N_{III} = (4\bar{Y}_T - \bar{H}_T)V_{III} + T_{Cu}^{III} + T_H^{III} . \qquad (135)$$

The sum of the concentrations of copper, ammonium, and hydrogen in the region 3 eluate which is transferred to the resin is $4\bar{Y}_T - \bar{H}_T$ because $\bar{H}_T$ and $\bar{Y}_T$ are the only quantities being transported through boundary III in the solution phase. Since

$$\overline{NH}_4 = 4\bar{Y}_T - \bar{H}_T \qquad (136)$$

and $$V_{III} = 1 - fN_{III} , \tag{137}$$

then $$N_{III} = \overline{NH}_4(1 - fN_{III}) + T_{Cu}^{III} + T_{H}^{III} . \tag{138}$$

As the elution progresses and the copper-ammonium-hydrogen equilibrium band builds up, the band will grow at just the rate at which the total equivalents of copper, ammonium, and hydrogen leak into the band ($T_{Cu}^{III} + T_{H}^{III} + T_{NH_4}^{II}$, where $T_{NH_4}^{II}$ is the rate at which ammonium is transported into region 3 through boundary II). Furthermore, if the concentrations are not to change as the band grows, the ratio of the equivalents of each species leaking into the band to that species already in the band must remain constant. If this is not initially true, there are sufficient degrees of freedom in the boundary transfers and equilibrium shifts so that these conditions can be fulfilled.

Copper-Ammonium-Hydrogen Band

It will be shown later that a rare-earth band inserted between boundary regions I and II will cause no difference in the compositions of the lower equilibrium bands or the transport of atomic species through the lower boundaries. The equilibrium rare-earth band will remain a constant length and composition; and any net transport of an atomic species into or out of the rare-earth band through the upper boundary region will be exactly equal to the net transport of that atomic species out of or into the band through the lower boundary region.

Since the region 3 (the copper-ammonium-hydrogen band) has attained equilibrium with the eluate, there will be no net transfer of ions between the solution and resin phases. As this band progresses, the N_{III} equivalents of cations which are laid down above boundary III must come from two sources; they are supplied by the V_{III} liters of eluate which enter the boundary region and by the net transport of ions which leak up through boundary III via the resin phase:

$$N_{III}E_{Cu} = 2Cu_TV_{III} + T_{Cu}^{III} \ , \qquad (139)$$

$$N_{III}E_{NH_4} = NH_4V_{III} \ , \qquad (140)$$

and

$$N_{III}E_H = (H_T - \bar{H}_T)V_{III} + T_H^{III} \qquad (141)$$

where

$$V_{III} = 1 - fN_{III} \ . \qquad (142)$$

The sum of the above three equations gives the following equation:

$$N_{III}(E_{Cu} + E_{NH_4} + E_H) = (2Cu_T + NH_4 + H_T - \bar{H}_T)V_{III} + T_{Cu}^{III} + T_H^{III} \ ; \qquad (143)$$

and, thus, $N_{III} = \overline{NH_4}_T(1 - fN_{III}) + T_{Cu}^{III} + T_H^{III}$. (144)

This equation is the same as was given for the rate at which the boundary III moved.

The atomic species which are present in the V_{II} liters of eluate which have passed boundary region II originated by being either transferred to the eluate from the resin or transported through the boundary in the solution phase. Copper and hydrogen which were originally on the resin in region 3 are transferred completely to the eluate in boundary region II and thus have no net transports through the boundary. Therefore,

$$2Cu_TV_{II} = 2Cu_T(1 - fN_{II}) = N_{II}E_{Cu} , \tag{145}$$

$$(H_T - \overline{H}_T)V_{II} = (H_T - \overline{H}_T)(1 - fN_{II}) = N_{II}E_H , \tag{146}$$

and

$$NH_4V_{II} = NH_4(1 - fN_{II}) = N_{II}E_{NH_4} + T^{II}_{NH_4} ; \tag{147}$$

and the sum of the above three equations gives rise to the following equation:

$$N_{II} = \overline{NH}_{4_T}(1 - fN_{II}) - T^{II}_{NH_4} . \tag{148}$$

This equation indicates the rate at which the boundary II is moving. When there is no rare-earth band between region 3 and region 1, the boundary region I below region 1 is identically the same as the boundary region II above region 3, therefore, N_{II} and N_I are the same.

The following equations are obtained by solving the equations above:

$$N_{II} = \frac{\overline{NH}_{4_T} - T^{II}_{NH_4}}{1 + f\overline{NH}_{4_T}} , \tag{149}$$

$$E_{Cu} = 2Cu_T(\frac{1}{N_{II}} - f) = \frac{2Cu_T(1 + fT^{II}_{NH_4})}{\overline{NH}_{4_T} - T^{II}_{NH_4}} , \tag{150}$$

$$E_{NH_4} = \frac{NH_4 - T^{II}_{NH_4}(1 + f\overline{NH}_{4_T} - fNH_4)}{\overline{NH}_{4_T} - T^{II}_{NH_4}} , \tag{151}$$

and
$$E_H = \frac{h_T(1 + fT^{II}_{NH_4})}{\overline{NH}_{4_T} - T^{II}_{NH_4}} . \tag{152}$$

There are two independent equilibria established between the eluate and the resin phases; namely,

$$Cu^{+2} + 2NH^+_{4_r} \rightleftharpoons 2NH^+_4 + Cu^{+2}_r ; \tag{153}$$

thus
$$K'_D = \frac{(NH_4)^2 \times E_{Cu}}{Cu \times E^2_{NH_4}} ; \tag{154}$$

and
$$NH^+_4 + H^+_r \rightleftharpoons H^+ + NH^+_{4_r} ; \tag{155}$$

thus
$$K'_F = \frac{H \times E_{NH_4}}{NH_4 \times E_H} . \tag{156}$$

When E_{Cu} and E_{NH_4} are eliminated from equation 154 by means of equations 150 and 151, the following equation is obtained:

$$Cu_T = Cu \times \frac{K'_D \; NH_4 - T^{II}_{NH_4}(1 + f\overline{NH}_{4_T} - fNH_4)^2}{2(\overline{NH}_{4_T} - T^{II}_{NH_4})(1 + fT_{NH_4})(NH_4)^2} ; \tag{157}$$

that is,
$$Cu_T = Cu \times g_2(NH_4, T^{II}_{NH_4}) . \tag{158}$$

When E_{NH_4} and E_H are eliminated from equation 156 by means of equations 151 and 152, the following equation is obtained:

$$h_T = H \times \frac{NH_4 - T^{II}_{NH_4}(1 + f\overline{NH}_{4T} - fNH_4)}{K'_F(1 + f\overline{NH}_{4T})NH_4} \; ; \qquad (159)$$

that is, $$h_T = H \times g_3(NH_4,\ T^{II}_{NH_4}) \qquad (160)$$

where $$h_T = H_T - \overline{H}_T \ . \qquad (161)$$

As is valid for the other bands, the concentration of each of the complexes in solution may be expressed in terms of the apparent equilibrium constants and the concentration of the simple ions H^+, Cu^{+2} and Y^{-4}. However, since the copper forms a very stable one to one complex with EDTA, it is not necessary to consider the extremely small amounts of H_4Y^0, H_3Y^-, H_2H^{-2}, HY^{-3}, and Y^{-4} in the eluate. The H_3Y^- ion has the largest concentration of these ions at the pH of the eluate in this band. Since

$$H_3Y = K'_2K'_3K'_4H^3 \times Y = 10^{20}\ H^3 \times Y \qquad (162)$$

and $$CuY = K'_ACu \times Y = 10^{19}\ Cu \times Y \qquad (163)$$

when $$H = 10^{-3} \text{ moles per liter} \qquad (164)$$

and $$Cu = 10^{-4} \text{ moles per liter,} \qquad (165)$$

then $$\frac{H_3Y}{CuY} = 10\,\frac{H^3}{Cu} = 10^{-4} \ . \qquad (166)$$

Therefore, each EDTA group may be considered to be complexed with one copper, and CuY^{-2} rather than Y^{-4} may be considered the simplest ion having an appreciable effect on the equilibrium established in this region.

Since very little EDTA is adsorbed anywhere along the column, generally, Y_T may be set equal to $\overline{Y}_T$. Thus,

$$\overline{Y}_T = Y_T = CuY + HCuY + H_2CuY \ , \qquad (167)$$

or
$$\overline{Y}_T = (1 + K_B'H + K_C'K_B'H^2)CuY \ . \qquad (168)$$

Furthermore, the following material balance equations are valid for the eluate in region 3:

$$H_T = \overline{H}_T + h_T = H + HCuY + 2H_2CuY \ ; \qquad (169)$$

thus,
$$\overline{H}_T + H \times g_3(NH_4, T_{NH_4}^{II}) - H = (K_B'H + 2K_C'K_B'H^2)CuY \ . \qquad (170)$$

$$Cu_T = Cu + CuY + HCuY + H_2CuY = Cu + \overline{Y}_T \ ; \qquad (171)$$

thus
$$Cu \times g_2(NH_4, T_{NH_4}^{II}) = Cu + \overline{Y}_T \ . \qquad (172)$$

The electroneutrality equation for region 3 may be written as follows:

$$NH_4 + 2Cu + H = 2CuY + HCuY \ ; \qquad (173)$$

therefore,
$$NH_4 + 2Cu + H = (2 + K_B'H)CuY \ . \qquad (174)$$

It may be observed at this point that there are the four equations 168, 170, 172, and 174 having the five unknown variables H, CuY, Cu, NH_4, and $T_{NH_4}^{II}$. The boundary conditions imposed at the upper boundary by the eluant band and all of the equations involved in the equilibrium band have been used. The only equation which has not been utilized is equation 134 which is the boundary condition imposed by the retaining bed. If this boundary condition will provide an equation employing only the variables included in the above list, then the composition of region 3 is completely determined. In order to show that this boundary condition may be transposed into a function with only five or fewer of the above variables, the following discussion was found necessary.

The solution of equations 139 and 145, 140 and 147, and 141 and 146 for $N_{III} - N_{II}$ gives the following equation:

$$N_{III} - N_{II} = \frac{T_{Cu}^{III}}{E_{Cu} + 2Cu_T f} = \frac{T_{NH_4}^{II}}{E_{NH_4} + NH_4 f} = \frac{T_H^{III}}{E_H + fh_T} \ . \qquad (175)$$

The above is certainly the expected result. The ratio of the rate that an atomic species is transported into a band to the quantity of this atomic species in a band containing one equivalent of resin should be the same for each atomic species in the band or the band would change composition and not be in equilibrium.

Equation 175 yields the following values for T_{Cu}^{III} and T_H^{III}:

$$T_{Cu}^{III} = \frac{T_{NH_4}^{II}(E_{Cu} + 2Cu_T f)}{E_{NH_4} + NH_4 f} \ , \qquad (176)$$

and

$$T_H^{III} = \frac{T_{NH_4}^{II}(E_H + h_T f)}{E_{NH_4} + NH_4 f} \ . \qquad (177)$$

When these equations were used to eliminate T_{Cu}^{III} and T_H^{III} from equation 134, the following equation is obtained (equation 134 is the boundary condition imposed by the retaining bed):

$$\frac{T^{II}_{NH_4}(E_{Cu} + 2Cu_Tf)}{E_{NH_4} + NH_4f} = \frac{E^*_{Cu} + 2Cu^*_Tf}{E^*_H + h^*_Tf}\left(h^*_T + T^{II}_{NH_4} \times \frac{E_H + h_Tf}{E_{NH_4} + NH_4f}\right) - 2Cu^*_T \; . \qquad (178)$$

The variable Cu_T was eliminated from equation 150 by means of equation 171 to obtain equation 179, and the variable h_T was eliminated from equation 152 by means of equation 160 to obtain equation 180, thus,

$$E_{Cu} = \frac{2(Cu + \overline{Y}_T)(1 + fT^{II}_{NH_4})}{\overline{NH}_{4_T} - T^{II}_{NH_4}} \; , \qquad (179)$$

and

$$E_H = \frac{(1 + fT^{II}_{NH_4}) \times H \times g_3(NH_4,\ T^{II}_{NH_4})}{\overline{NH}_{4_T} - T^{II}_{NH_4}} \; . \qquad (180)$$

When the variables E_{Cu}, E_H, E_{NH_4}, Cu_T, and h_T are eliminated from equation 178 by means of equations 179, 180, 151, 171, and 160, respectively, the resulting equation has only the four variables H, Cu, NH_4, and $T^{II}_{NH_4}$. Therefore, when this equation is added to the list of equations which are enumerated on page 80, there are five independent equations and five unknown variables H, CuY, Cu, NH_4, and $T^{II}_{NH_4}$. Thus, the composition of the eluate and resin phase of region 3 may be completely established from the eluant composition, the retaining bed composition, and the apparent equilibrium constants of the system.

Neodymium-Ammonium-Hydrogen Band

If a pure rare-earth band is inserted between the eluant band and the region 3, dilution of the rare-earth with ammonium and hydrogen would occur in the same fashion as occurred in the elution of the rare-earth band with the ammonia buffered citrate eluant and the hydrogen retaining bed. Initially, more ammonium and hydrogen will be transported in the top boundary than is transported out the bottom boundary. The band will grow until an equilibrium length is obtained.

Since there is a constant amount of rare-earth in the band, there must be a constant amount of ammonium and hydrogen in the equilibrium rare-earth band. Therefore, once equilibrium has been attained, the net transport of ammonium ions in the top of the band must be the same as the net transport of ammonium out the bottom of the band; namely, the transport necessary to maintain the equilibrium copper-ammonium-hydrogen band. Because of the boundary conditions imposed at the upper boundary, the $\overline{\overline{H}}_T$ in the eluant will be transported down through both boundaries.

An atomic species leaving boundary region I in the V_I liters of eluate is either transferred from the N_I equivalents of resin or transported from the eluant band into the eluate through the boundary I. Thus,

$$3Nd_TV_I = N_IE_{Nd} , \tag{181}$$

$$NH_4V_I = N_IE_{NH_4} + T^I_{NH_4} , \tag{182}$$

and $$(H_T - \overline{H}_T)V_I = N_I E_H \ . \tag{183}$$

The rate at which boundary I moves was given previously by equations 43 and 44; that is,

$$N_I = \frac{\overline{NH}_{4_T} - T^I_{NH_4}}{1 + f\overline{NH}_{4_T}} \ , \tag{184}$$

and $$V_I = 1 - fN_I \ . \tag{185}$$

When V_I and N_I are eliminated from equations 181, 182, and 183 by means of equations 184 and 185, the following equations are obtained:

$$E_{Nd} = \frac{3Nd_T(1 + fT^I_{NH_4})}{\overline{NH}_{4_T} - T^I_{NH_4}} \ , \tag{186}$$

$$E_{NH_4} = \frac{NH_4 - T^I_{NH_4}(1 + f\overline{NH}_{4_T} - fNH_4)}{\overline{NH}_{4_T} - T^I_{NH_4}} \ , \tag{187}$$

and $$E_H = \frac{h_T(1 + fT^I_{NH_4})}{\overline{NH}_{4_T} - T^I_{NH_4}} \tag{188}$$

where $$h_T = H_T - \overline{H}_T \ . \tag{189}$$

The following equilibria occur between the eluate and the resin phase:

$$Nd^{+3} + 3NH^+_{4_r} \rightleftharpoons 3NH^+_4 + Nd^{+3}_r \ ; \tag{190}$$

thus, $$K'_I = \frac{(NH_4)^3 \times E_{Nd}}{Nd \times (E_{NH_4})^3} \ ; \tag{191}$$

and $$NH_4^+ + H_r^+ \rightleftharpoons H^+ + NH_{4_r}^+ \; ; \qquad (192)$$

thus, $$K'_F = \frac{H \times E_{NH_4}}{NH_4 \times E_H} \; . \qquad (193)$$

When the variables E_{Nd}, E_{NH_4}, and E_H are eliminated from equations 191 and 193, the following equations are obtained:

$$Nd_T = Nd \times \frac{K'_I(NH_4 - T^I_{NH_4}\ 1 + f\overline{NH}_{4_T} - fNH_4\ )^3}{3(1 + fT^I_{NH_4})(\overline{NH}_{4_T} - T^I_{NH_4})^2(NH_4)^3} \; ; \qquad (194)$$

therefore, $$Nd_T = Nd \times g_4(NH_4) \; ; \qquad (195)$$

and $$h_T = H \times \frac{NH_4 - T^I_{NH_4}(1 + f\overline{NH}_{4_T} - fNH_4)}{K'_F(1 - fT^I_{NH_4})NH_4} \; ; \qquad (196)$$

therefore, $$h_T = H \times g_5(NH_4) \; . \qquad (197)$$

The variables $g_4(NH_4)$ and $g_5(NH_4)$ are functions of the unknown variable NH_4.

The following equilibria are established in the eluate of the neodymium band:

$$Nd^{+3} + Y^{-4} \rightleftharpoons NdY^- \; , \qquad (198)$$

and $$K'_G = \frac{NdY}{Nd \times Y} \; , \qquad (199)$$

or $$NdY = K'_G Nd \times Y \; ; \qquad (200)$$

$$H^+ + NdY^- \rightleftharpoons HNdY^0 \; ; \qquad (201)$$

and $$K'_H = \frac{HNdY}{H \times NdY} \; , \qquad (202)$$

or
$$HNdY = K'_H K'_G H \times Nd \times Y \ . \tag{203}$$

Since very little EDTA goes into the resin, Y_T may be set equal to $\overline{Y}_T$ without making too large an error. However, if the nature of any adsorption of EDTA by the resin is known, corrections could be made.

$$Y_T = NdY + HNdY + H_4Y + H_3Y + H_2Y \ , \tag{204}$$

and

$$\overline{Y}_T = (K'_G Nd + K'_H K'_G H \times Nd + K'_1 K'_2 K'_3 K'_4 H^4 + K'_2 K'_3 K'_4 H^3 + K'_3 K'_4 H^2) Y. \tag{205}$$

The concentrations of HY^{-3} and Y^{-4} may generally be ignored in the material balance at the pH involved in the rare-earth band. The variables Nd_T and h_T may be eliminated from the material balance equations by means of equations 195, 189, and 197; then,

$$Nd_T = Nd + NdY + HNdY \ ; \tag{206}$$

thus,
$$Nd \times g_4(NH_4) = Nd + K'_G Nd \times Y + K'_H K'_G H \times Nd \times Y \ ; \tag{207}$$

and
$$H_T = \overline{H} + h_T = H + HNdY + 4H_4Y + 3H_3Y + 2H_2Y \ ; \tag{208}$$

thus,

$$\overline{H}_T + H \times g_5(NH_4) = H + (K'_H K'_G H \times Nd + 4K'_1 K'_2 K'_3 K'_4 H^4 + 3K'_2 K'_3 K'_4 H^3 + 2K'_3 K'_4 H^2) Y \ . \tag{209}$$

The equation expressing the electrical neutrality of the eluate may be written as follows:

$$NH_4 + 3Nd + H = NdY + H_3Y + 2H_2Y \ ; \tag{210}$$

therefore,

$$NH_4 + 3Nd + H = (K'_G Nd + K'_2 K'_3 K'_4 H^3 + 2K'_3 K'_4 H^2)Y \ . \qquad (211)$$

Since equations 205, 207, 209, and 211 have only the unknowns H, Nd, Y, and NH_4, the values of these unknowns are established, and the complexes may be calculated using the appropriate apparent constants. The composition of the eluate and resin phase may be calculated by using the material balance equations and the equations expressing the material balance at the boundary.

Thus, it has been shown that the compositions of both phases of the regions 1, 2, 3, and 4 and the net transports at the various boundaries are determined by the composition of the eluant, the composition of the resin retaining bed, and the apparent equilibrium constants of the system after equilibrium has been established in all of the bands.

RESEARCH AND RESULTS OF EQUILIBRIUM STUDIES

It has been shown in the theoretical developments discussed in this thesis that the elution system is predetermined by a given eluant and a given retaining bed. For the n unknowns in the system, n equations may be written which involve the concentrations of the ions, the equivalent fractions of the various ions on the resin and the transport occurring at the m boundaries of the bands. If these equations are to be solved simultaneously for the various concentrations and equivalent fractions, it is necessary to know the apparent stability constants of the various complex ions and the apparent equilibrium constants for the exchange of cationic species between the solution and resin phases. While one constant in an elution experiment may be calculated for each concentration determined experimentally, it is desirable in practice to check these relationships by independently determining a few of these apparent equilibrium constants by means of batch operations wherein the eluate has the same ionic strength and the resin has the same equivalent fractions as the equilibrium bands.

It should be mentioned that some of the apparent constants and some of the ionic species which are present in very low concentrations can not be calculated with great precision from elution data using the ionic concentrations usually measured. Since the set of equations being solved involves both material balance equations and equilibrium equations, they do not contain exact numbers but rather measure quantities which are subject to experimental error. Therefore, in solving for low concentrations of ions or for apparent equilibrium constants which involve either the product or quotient of two or more of these quantities, the results are drastically influenced by the experimental error. The best that can be done is to obtain as precise a value as possible for the product or quotient of these particular quantities. It is best that these particular constants should be determined independently or taken from the literature.

The main purpose of this thesis was to establish theoretically and experimentally that equilibrium band systems could be maintained with various retaining resin bed compositions. However, it seemed desirable to determine approximately a few of the equilibrium constants under specific conditions in order to ascertain whether or not the theory was in reasonable agreement with the experimental results. The intriguing possibility that these systems along with the theory could be used for the precise determination of these constants remains to be established and suggests an interesting problem for future work.

Copper-Ammonium-Hydrogen-Solution-Resin Equilibria

Six equilibrium experiments were performed as follows. The copper-ammonium-hydrogen-band resin was prepared by weighing three different forms of resin (copper, ammonium, and hydrogen) into a vessel. The air-dried resin was brought to equilibrium with a copper-ammonium-hydrogen-band eluate. Also, an appropriate volume of water which was calculated to be the amount imbibed by the resin in its swollen state was added with the eluate. Since the initial and final compositions of the eluate were determined by analysis, the final composition of the resin could be computed by correcting the initial composition of the resin by the amount of copper, ammonium, and hydrogen removed from or transferred to the eluate by the resin.

The resin used in these experiments as well as in elutions 27, 28, and 29 was taken from the same sample of Amberite IR-120 resin. The air-dried copper- and hydrogen-saturated resins were each prepared in the identical manner described on page 26. An ammonium chloride solution was used to prepare the ammonium-saturated resin. After the resin had been washed with deionized water and air-dried, a concentrated solution of sodium chloride was used to strip the ammonium ion from a weighed sample of the resin into a volumetric flask. Then the contents of the flask were diluted to the mark, and aliquots were analyzed to determine the equivalents of ammonium per gram of resin (e_{NH_4}). The procedure for determining the equivalents of copper per gram of resin (e_{Cu}) and the equivalents of hydrogen per gram of resin (e_H) is indicated on page 27.

$$e_{Cu} = 0.003497 \ , \tag{212}$$

$$e_{NH_4} = 0.004180 \ , \tag{213}$$

and

$$e_H = 0.004100 \ . \tag{214}$$

The number of milliliters of water adsorbed by a gram of resin was estimated in the following manner. A weighed quantity of one of the three resins was added to a known volume of a solution having a known concentration of the cation with which the resin was saturated. After the resin and the solution were mixed together for two days, the concentration of the cation in the equilibrated solution was determined.

The quantity of salt imbibed in the resin was estimated from data given by Gregor (6) for similar conditions and resin in both the hydrogen cycle and the ammonium cycle. Since copper sulfate solution was used to equilibrate the copper resin and appropriate data were not available in the literature, the amount of salt imbibed in the resin was determined experimentally by centrifuging the equilibrated solution from the resin phase, leaching the resin with deionized water, and determining the quantity of copper sulfate in the water.

Since the product of the volume times the concentration of the salt in the external solution before equilibration is equal to the sum of the salt in the resin phase and the product of the volume times the concentration of the salt after equilibration, the volume of the solution after equilibration may be estimated from the data indicated above. If the difference in the volumes before and after equilibration is divided by the grams of resin used, an estimate of the number of milliliters of water adsorbed per gram of resin, $(ml/g)_i$, is obtained:

$$(ml/g)_{Cu} = 0.496 \;, \tag{215}$$

$$(ml/g)_{NH_4} = 0.711 \;, \tag{216}$$

and

$$(ml/g)_{H} = 0.794 \;. \tag{217}$$

It should be noted that an air-dried resin already contains some water before it is contacted with a solution.

The eluate used in these equilibrations was prepared by performing elutions which were very similar to the elutions described previously in this thesis. The difference was that only the homogeneous copper-ammonium-hydrogen band was used (3). As before, the ammonia-buffered EDTA solution was used as the eluant. In the central portion of the copper-ammonium-hydrogen band, the eluate phase achieved almost complete equilibrium with the resin phase. Eluate samples from this portion of the band were combined and mixed for each elution. Each of these composite eluates was analyzed for the concentrations of ammonium ions (NH_4), of the total replaceable hydrogen (H_T), and of the copper in excess of the one to one complex with EDTA (Cu_E).

Since the concentration of the total copper consists of that forming the one to one complex and that in excess of this complex,

$$Cu_T = Y_T + Cu_E \; . \qquad (218)$$

The electroneutrality of the solution requires that

$$4Y_T = 2Cu_T + NH_4 + H_T \; . \qquad (219)$$

When Cu_T is eliminated from equation 219 by means of equation 218, then the following equation is obtained which allows Y_T to be evaluated from the data indicated above.

$$Y_T = Cu_E + \frac{NH_4 + H_T}{2} \; . \qquad (220)$$

Thus, Cu_T may be evaluated by means of equation 218.

A volume of v liters of this eluate and L_T' liters of water were added to a two-liter Erlenmeyer flask containing G_{Cu} grams of copper-form resin, G_{NH_4} grams of ammonium-form resin, and G_H grams of the hydrogen-form resin. The flask was closed with a rubber stopper and supported above the table top by means of a clamp and a ring stand. A type of magnetic stirrer was used to continually mix the solution and resin. It was constructed by placing a round bar magnet through a tight fitting hole in the top of a cork and inserting the shaft of a small electric motor into a tight fitting hole in the center of the cork and perpendicular to the magnet. The electric motor was clamped below the flask such that the magnet rotated in a horizontal plane just beneath the bottom of the flask. A small bar magnet, enclosed in glass tubing which was sealed at both ends, was used within the flask. A fan was directed on the motor to keep the motor from heating the flask. A commercial stirrer could not have been cooled so easily. The stirrer was adjusted to a rate which kept the contents of the flask mixing continually.

After three days of stirring, aliquots of the eluate were analyzed for the ammonium concentration (NH_4^x), the total replaceable hydrogen (H_T^x), and the copper concentration in excess of the one to one complex with EDTA (Cu_E^x). The value of Y_T^x and Cu_T^x were calculated from equations 220 and 218.

The liters of water adsorbed by the resin are L_T:

$$L_T = \frac{G_{Cu}(ml/g)_{Cu} + G_{NH_4}(ml/g)_{NH_4} + G_H(ml/g)_H}{1000} . \qquad (221)$$

The volume of the eluate just after equilibration (v^x) is given by the following equation:

$$v^x = v + L_T^{'} - L_T . \qquad (222)$$

The total equivalents of cations in the resin phase before the eluate was placed in the flask were Q_T equivalents:

$$Q_T = G_{Cu}e_{Cu} + G_{NH_4}e_{NH_4} + G_He_H . \qquad (223)$$

The moles of EDTA in the resin phase per equivalent of resin (δ_4) after the resin was equilibrated with eluate are given by the following expression:

$$\delta_4 = \frac{Y_T v - Y_T^x v^x}{Q_T} . \qquad (224)$$

The equivalents of cations in the resin phase after the resin has reached equilibrium with the eluate (Q_T^x) is given by the following equation:

$$Q_T^x = Q_T(1 + 4 \quad _4) . \qquad (225)$$

Equating the sum of the equivalents of copper in the eluate and the equivalents in the resin before equilibrium to the sum of the equivalents of copper in the eluate and the equivalents in the resin phase after equilibrium and solving for the equivalents of copper in the resin phase after equilibrium (Q_{Cu}^x), the following equation is obtained:

$$Q_{Cu}^x = G_{Cu} e_{Cu} + 2v \cdot Cu_T - 2v^x \cdot Cu_T^x . \qquad (226)$$

Similarly,

$$Q_{NH_4}^x = G_{NH_4} e_{NH_4} + v \cdot NH_4 - v^x \cdot NH_4^x , \qquad (227)$$

and

$$Q_H^x = G_H e_H + v \cdot H_T - v^x \cdot H_T^x . \qquad (228)$$

After equilibrium, the equivalents of copper per equivalent of resin (E_{Cu}^x) is given by the following equation:

$$E_{Cu}^x = \frac{Q_{Cu}^x}{Q_T^x} . \qquad (229)$$

Similarly,

$$E_{NH_4}^x = \frac{Q_{NH_4}^x}{Q_T^x} , \qquad (230)$$

and

$$E_H^x = \frac{Q_H^x}{Q_T^x} . \qquad (231)$$

The data for six equilibrium experiments are given in Table 2.

In the theoretical discussion, it was shown that when the cationic species are forced to deposit at the front boundary of the copper-ammonium-hydrogen band by the copper-hydrogen retaining bed, then the eluate comes to equilibrium with the resin phase in this region 3. If no copper-hydrogen retaining bed is used, it takes longer for the copper-ammonium-hydrogen band to come to equilibrium. However, if the eluate is initially in equilibrium with the resin phase in region 3, then no addition elution time will be required to achieve equilibrium.

For a suitable eluant of fixed composition and for a predetermined leak through of ammonium at boundary II, the theory shows that only one composition of resin can be in equilibrium with the eluate such that an equilibrium band is maintained. Thus, the compositions of the resin and the eluate for the case of no transport of ammonium were calculated for the eluant 20 (see Table 3). In order to make these calculations, a resin bed of arbitrary composition believed to be near the value sought was brought to equilibrium with the eluant 20 by an elution experiment. The eluate from this experiment was then brought to equilibrium with an air-dried

Table 2a. Equilibrium studies on the copper-ammonium-hydrogen band

Experiment no.	Eluate concentration before equilibrium[a]							Resin composition before equilibrium		
	NH_4	H_T	Cu_E	pH	Y_T	Cu_T	L'_T	G_{Cu}	G_{NH_4}	G_H
E-3	0.02192	0.00650	0.000543	3.45	0.01475	0.01530	0.1216	168.50	96.40	2.200
E-4	0.02666	0.00288	0.000705	3.92	0.01548	0.01618	0.1219	157.62	107.50	0.2977
E-5	0.02745	0.01256	0.000119	3.225	0.02119	0.02238	0.1209	172.63	93.23	1.610
E-6	0.02192	0.00650	0.000543	3.45	0.01475	0.01530	0.1222	167.07	97.35	1.473
E-7	0.01062	0.00472	0.000453	3.335	0.008124	0.008577	0.1037	170.09	92.19	4.834
E-8	0.02180	0.00648	0.000611	3.45	0.01475	0.01536	0.0839	131.16	80.15	1.102

[a] $v = 1.500$ liters.

Table 2b. Equilibrium studies on the copper-ammonium-hydrogen band

Experiment no.	Eluate concentration after equilibrium							Resin composition after equilibrium		
	NH_4^x	H_T^x	Cu_E^x	pH^x	Y_T^x	Cu_T^x	δ_4	E_{Cu}^x	$E_{NH_4}^x$	E_H^x
E-3	0.02065	0.00751	0.000586	3.36	0.01467	0.01525	0.0006	0.5882	0.4041	0.00771
E-4	0.02724	0.00235	0.000763	3.975	0.01555	0.01632	0.0004	0.5500	0.4479	0.00209
E-5	0.02745	0.01197	0.00120	3.245	0.02091	0.02211	0.0011	0.6033	0.3889	0.00782
E-6	0.02210	0.00639	0.000588	3.44	0.01483	0.01542	0.0003	0.5857	0.4079	0.00641
E-7	0.01046	0.00619	0.000110	3.17	0.008445	0.008545	(0.0000)	0.5959	0.3862	0.01796
E-8	0.02219	0.00634	0.000588	3.47	0.014851	0.01544	0.0005	0.5746	0.4192	0.00622

Table 3. Elution 24 with an eluant 0.014736 molar in EDTA and 0.05279 molar in total ammonium

	Eluate samples from copper-ammonium-hydrogen band First	Second	Fifth	Eighth	Theoretical composition for no transport
Cu_E	0.000597	0.00613	0.000618	0.000619	0.00060
H_T	0.006531	0.00645	0.006477	0.006482	0.00650
NH_4	0.021775	0.02179	0.02184	0.02180	0.02177
$T^{II}_{NH_4}$	0.0004	0.0004	0.0004	0.0004	0.0000
Y_T	(0.01475)	(0.01473)	(0.01477)	(0.01476)	0.014736[a]
Cu_T	(0.01535)	(0.01535)	(0.01539)	(0.01538)	0.01534
pH	3.45	3.45	3.45	3.46	3.44
$H\times10^4$	4.03	4.03	4.03	3.94	4.13
h_T	0.00038	0.00030	0.00032	0.00033	0.00035
E_{Cu}	(0.5857)	(0.5857)	(0.5857)	(0.5857)	0.5810
E_{NH_4}	(0.4079)	(0.4079)	(0.4079)	(0.4079)	0.4124
E_H	(0.0064)	(0.0064)	(0.0064)	(0.0064)	0.0066

[a] Y_T is assumed the same as $\overline{Y}_T$ of the eluant.

resin chosen to give the crudely estimated composition of the equilibrium resin. After equilibrium was attained, the solution was analyzed as previously and the apparent equilibrium constants for the various equilibria were calculated. These constants were then used to calculate the composition of the initial resin used in E-6 which was brought to equilibrium with the same eluate. Again the solution was analyzed and more exact apparent equilibrium constants were calculated. Even in this case, there was a small shift from the equilibrium expected, but the shift was small enough that the calculated apparent equilibrium constants would not be much different for the idealized case.

Eluant 20 and the resin from experiment E-6 were used in an elution to ascertain whether these compositions would result in no leak through of ammonium and whether the composition of the equilibrium eluate was close to the composition calculated from the eluant using the apparent equilibrium constants in the batch equilibration experiments. The elution was carried out as follows. A glass column, approximately 2.2 centimeters in diameter and 120 centimeters in length, was filled with part of the remaining eluate and all of the resin was allowed to settle through the eluate into an evenly packed resin bed. The eluate was allowed to flow out the bottom of the column until the liquid was level with the top of the resin bed. After carefully filling the column with eluant 20, the eluant was allowed to flow into the top of the column while two-liter samples of the eluate were collected from the bottom of the column at the flow rate of one milliliter per minute by means of the bottle changer.

Several of these eluate samples from the copper-ammonium-hydrogen band were analyzed for the same components whose concentrations were determined in the equilibrium experiments previously mentioned. The results are given in Table 3.

Since the eluate flowing from the column has virtually a constant composition, there is apparently little net transfer between the resin and the solution phases, and the resin composition in the copper-ammonium-hydrogen band remains virtually the same as the initial resin composition (It is the final resin composition of E-6 given in Table 2). Eluant 20 had a total ammonium concentration of 0.05279 and a total EDTA concentration of 0.014736.

The apparent net equivalents of ammonium which are transported down through the upper boundary of the copper-ammonium-hydrogen band as one liter of the eluant passes in the top of the column ($T^{I}_{NH_4}$) is given by equation 260. Table 3 shows that the net transport of ammonium through the boundary is about one-fiftieth of the ammonium concentration in the copper-ammonium-hydrogen eluate and is a constant value. Thus, this elution indicates that these constants may be used to determine to better than one percent the composition of an equilibrium copper-ammonium-hydrogen band.

Neodymium-Ammonium-Hydrogen-Solution-Resin Equilibria

Three equilibrium experiments were performed in an exactly analogous manner as the equilibrium studies on the copper-ammonium-hydrogen band. The resin for the neodymium-ammonium-hydrogen band was prepared by weighing the three different forms of resin (neodymium, ammonium, and hydrogen) into a vessel. This resin was brought into equilibrium with a neodymium-band eluate plus a designated number of milliliters of water by stirring the mixture in a closed Erlenmeyer flask. The final resin composition is calculated in the manner indicated in the previous section.

The ammonium- and hydrogen-form resins were the same as used in the equilibrium studies on the copper-ammonium-hydrogen band. The air-dried, neodymium-form resin was prepared in the manner indicated on page 26. Neodymium chloride was used to saturate the resin. The equivalents of neodymium per gram of this resin (e_{Nd}) and the milliliters of water taken up by a gram of this resin $(ml/g)_{Nd}$ were determined in the same way as these values were obtained for the copper-form resin which was indicated on pages 26, 94, and 95.

$$e_{Nd} = 0.003230 \,, \tag{232}$$

and

$$(ml/g)_{Nd} = 0.312 \,. \tag{233}$$

The eluate used in equilibrium E-9 was prepared by combining several of the neodymium-band-eluate samples from elution 27, and the eluate used in equilibrium E-11 was prepared by combining several of the neodymium-band-eluate samples from elution 28. Then, equal volumes of the eluates used in E-9 and E-11 were combined to produce the eluate used in E-10. The compositions of the eluates used in E-9, E-10, and E-11 were calculated from the individual volumes and the compositions of the samples constituting the composite eluates. Each of the samples from elutions 27 and 28 were analyzed for the concentration of ammonium (NH_4), the total neodymium concentration (Nd_T), and the concentration of EDTA in excess of the one to one complex with neodymium (Y_E). The total EDTA concentration (Y_T) and the total replaceable hydrogen (H_T) may be calculated using the following equations:

$$Y_T = Nd_T + Y_E \tag{234}$$

$$H_T = Nd_T + 4Y_E - NH_4. \tag{235}$$

The equilibration mixture was prepared in the same fashion as the copper-ammonium-hydrogen band batch equilibration; that is, a volume of v liters of the eluate and L_T' liters of water were added to the Erlenmeyer flask containing the designated grams of neodymium-, ammonium-, and hydrogen-form resin, G_{Nd}, G_{NH_4}, and G_H, respectively. The mixture was agitated in exactly the same way as in the previous equilibrium experiments.

After equilibrium was attained, aliquots of the eluate were analyzed for the concentration indicated above for the original eluate; namely, NH_4^x, Nd^x, and Y_E^x. The Y_T^x and the H_T^x are calculated by means of equations 234 and 235.

Many of the equations used in the calculations are analogous to the equations used in the equilibrium section on the copper-ammonium-hydrogen band.

The volume of water adsorbed by the resin L_T is given by equation 221 when $G_{Cu}(ml/g)_{Cu}$ is replaced by $G_{Nd}(ml/g)_{Nd}$. The volume of the eluate immediately after equilibrium (v^x) is given by equation 222. The total number of equivalents of cations in the resin phase before the eluate was placed in the flask is given by equation 223 when $G_{Cu}e_{Cu}$ is replaced by $G_{Nd}e_{Nd}$. The number of moles of EDTA in the resin phase per equivalent of resin in equilibrium with the eluate (δ_4) is given by equation 224 and the equivalents of cations in the resin phase after the resin has come to equilibrium with the eluate (Q_T^x) are given by equation 225. The number of equivalents of neodymium in the resin after equilibrium is attained (Q_{Nd}^x) is given by the following equation:

$$Q_{Nd}^x = G_{Nd}e_{Nd} + 3v \cdot Nd_T - 3v^x \cdot Nd_T^x \; . \qquad (236)$$

The number of equivalents of ammonium and hydrogen in the resin, after equilibrium is established, is given by equations 228 and 229, respectively.

The number of equivalents of neodymium per equivalent of resin after equilibrium is established is given by the following expression:

$$E_{Nd}^x = \frac{Q_{Nd}^x}{Q_T^x} \; . \qquad (237)$$

The equivalents of ammonium and hydrogen per equivalent of resin are given by equations 230 and 231, respectively.

The experimental data is given in Table 4.

Table 4a. Equilibrium studies on the neodymium-ammonium-hydrogen band

Experiment no.	Eluate concentration before equilibrium							Resin composition before equilibrium		
	NH_4	Nd_T	Y_E	pH	Y_T	H_T	L'_T	G_{Nd}	G_{NH_4}	G_H
E-9	0.015465	0.014995	0.001077	3.27	0.01607	0.00384	0.0576	114.90	30.00	0.8724
E-10	0.013884	0.011710	0.002092	--	0.01380	0.00619	0.0593	108.82	34.46	1.090
E-11	0.012308	0.008425	0.003117	3.235	0.01164	0.00859	0.0607	102.70	38.90	1.311

Table 4b. Equilibrium studies on the neodymium-ammonium-hydrogen band

Experiment no.	Eluate concentration after equilibrium							Resin composition after equilibrium		
	NH_4^x	Nd_T^x	Y_E^x	pH^x	Y_T^x	H_T^x	δ_4	E_{Nd}^x	$E_{NH_4}^x$	E_H^x
E-9	0.01385	0.01326	0.000828	3.37	0.01409	0.00272	0.002363	0.74125	0.25034	0.00841
E-10	0.01295	0.01087	0.001759	3.31	0.01263	0.00496	0.001874	0.70177	0.28740	0.01083
E-11	0.01173	0.00804	0.002771	3.30	0.01081	0.00740	0.00146	0.66225	0.32469	0.01306

Potentiometric Titrations of EDTA

The four stability constants of ethylenediaminetetraacetic acid were determined at three ionic strengths. Standard solutions of a potassium salt of ethylenediaminetetraacetate whose ionic strengths are largely determined by a known amount of potassium chloride were first titrated potentiometrically with standard potassium hydroxide solution to determine K_3' and K_4'. In order to determine K_1' and K_2', additional samples were titrated with standard hydrochloric acid solutions. (See page 54 for the definitions of K_1', K_2', K_3', and K_4').

The activity coefficients were determined at the various ionic strengths by measuring the pH of a number of standard hydrochloric acid solutions which were of a known ionic strength and contained mostly potassium chloride. The hydrogen-ion concentrations for the titration curves were determined from the pHs observed and the appropriate activity coefficients.

The charge-balance equation, the EDTA-total equation, the ionization equation for water, and the definitions of K_1', K_2', K_3', and K_4' were used in calculating the four constants from the titration curve.

Materials

A potassium salt of EDTA was prepared in a manner completely analogous with the procedure given in a previous section for the preparation of $(NH_4)_2H_2Y$. A stock solution was prepared by adding 22.1 grams of this salt to a two-liter flask and diluting the contents to the mark. Aliquots of this solution were titrated with a standard zinc chloride solution. The concentration of EDTA in the stock solution was 0.02645 molar, and the subsequent titrations showed that the stock solution had the composition of $K_{2.404}H_{1.596}Y$.

The potassium chloride used in preparing a 1.00 molar stock solution was precipitated from a saturated solution of potassium chloride by the addition of concentrated hydrochloric acid. The precipitated salt was fused to remove the water. A portion of the potassium chloride was then weighed into a volumetric flask, and the contents were diluted to the mark.

Five solutions were prepared by pipetting aliquots of the potassium chloride and EDTA stock solutions into a liter volumetric flask and diluting the contents to the mark. The first solution was prepared by diluting 100 milliliters of each of the two stock solutions, the second by diluting 35 milliliters of each of the two stock solutions, and the third by diluting 10 milliliters of each of the two stock solutions to 1000 milliliters. A pH meter was used to titrate 100 milliliter aliquots of each of these three solutions with a standard potassium hydroxide solution to obtain the titration curves of pH versus milliliters of base added. Also, an 100 milliliter aliquot of the first solution was titrated with a standard hydrochloric acid solution. A fourth solution was prepared by pipetting 100 milliliters of the EDTA stock solution and 25 milliliters of the potassium chloride solution into a liter volumetric flask and diluting the contents to the mark. One hundred milliliters of the EDTA stock solution were diluted to 1000 milliliters to prepare the fifth solution. The pH meter was used to titrate 100 milliliter aliquots of the fourth and fifth solutions with a standard hydrochloric acid solution to determine the titration curves.

The carbonate-free hydroxide solution was prepared by passing a potassium hydroxide solution through a hydroxide-form, anion-exchange column. The hydroxide-form exchange column was prepared by passing a solution of sodium hydroxide containing barium hydroxide through the column. The barium hydroxide was originally added in excess to precipitate any carbonate ions as barium carbonate. The sodium and barium ions are removed subsequently by washing the column with deionized water.

The potassium hydroxide solutions were standardized with potassium acid phthalate and the acid solutions were standardized with the potassium hydroxide solutions.

Apparatus

The titrations were carried out in a double-walled titration cell. The water which was maintained at 25.00° C ± 0.02° in a constant temperature bath was pumped through the jacketed compartment of the titration cell. An atmosphere of pure nitrogen was maintained above the liquid in the titration cell.

The more accurate Beckman Model G-S pH meter was used for these titrations rather than the Beckman Model G pH meter, and the electrode system consisted of a fiber type saturated calomel electrode and a "General Purpose" glass electrode. Both electrodes were of the shielded type for use external to the pH meter. A Pyrex microburette with 0.01 milliliter subdivisions was used to measure the volume of potassium hydroxide solution or hydrochloric acid solution used in the titrations.

Procedure

The pH meter was standardized with Beckman pH 4 buffer for the titrations of EDTA with hydrochloric acid. Both a standardization with the Beckman pH 7 buffer and then standardizations with the Beckman pH 9 buffer were necessary to cover the complete range in the titrations with the base because the pH meter only covered a range of three pH units with each standardization.

Since the pH as obtained from the pH meter thus standardized is defined in terms of the hydrogen-ion activity, while hydrogen-ion concentration (H) is needed for the calculations, it was necessary to correct the pH meter readings. The results shown in Table 5 were obtained for pH + log HCl where HCl represents the molar concentration of the hydrochloric acid in a solution whose potassium chloride concentration contributes the major portion of the ionic strength.

Table 5. pH-meter correction and the ionization constant of water

μ	pH + log HCl	$K_w' \times 10^{14}$
0.00	--	1.016
0.01	0.048	1.244
0.04	--	1.446
0.05	0.057	--
0.09	--	1.613
0.10	0.080	--
0.12	0.094	--
0.16	--	1.741

Since the hydrochloric acid may be considered to be completely ionized, the hydrogen-ion concentration is equal to the molar concentration of the hydrochloric acid. Therefore, the value of pH + log HCl for the appropriate ionic strength was subtracted from the pH given by the pH meter in the titrations in order to obtain -log H.

$$-\log H = pH - (pH + \log HCl) \qquad (238)$$

The $K_w^{'}$ in Table 5 is the ionization constant of water (69).

The titration curve of EDTA with a standard potassium hydroxide solution has two distinct inflection points, one at $\underline{a} = 2$ and the other at $\underline{a} = 3$, where $\underline{a}$ represents the fraction of the total replaceable hydrogen which has been titrated. The inflection point at $\underline{a} = 1$ is absent because K_1 and K_2 have about the same strength. There is no inflection at $\underline{a} = 4$ due to extensive hydrolysis of tetravalent ion.

By definition, the potassium-ion concentration which is not contributed from potassium chloride is the product of $\underline{a}$ and Y_T. Thus the following charge balance equation is obtained (see page 47 for definitions of the symbols):

$$H + aY_T = OH + H_3Y + 2H_2Y + 3HY + 4Y \ . \qquad (239)$$

The total EDTA concentration is of course equal to the sum of the concentration of the individual ions.

$$Y_T = H_4Y + H_3Y + H_2Y + HY + Y \qquad (240)$$

When the EDTA ions in equations 239 and 240 are replaced by functions of Y, H, $K_1^{'}$, $K_2^{'}$, $K_3^{'}$, and $K_4^{'}$ which are formed from the definitions of the four constants, and Y is eliminated between equations 239 and 240, then the following result is obtained:

$$a' = \frac{H^3K_2'K_3'K_4' + 2H^2K_3'K_4' + 3HK_4' + 4}{H^4K_1'K_2'K_3'K_4' + H^3K_2'K_3'K_4' + H^2K_3'K_4' + HK_4' + 1} \qquad (241)$$

where $$a' = a + \frac{H - K_w/H}{Y_T} . \qquad (242)$$

If the terms having H^4 and H^3 are ignored, since they are extremely small when K_4' is most important, then one obtains equation 243 when the equation 241 is solved for K_4'.

$$K_4' = \frac{4 - a'}{(a' - 3)H + (a' - 2)H^2K_3'} . \qquad (243)$$

It is only necessary to use a rough approximation of K_3' as it has only a small effect on K_4' in the region of $\underline{a}' = 3.5$.

If the terms having H^4 are ignored, since they are extremely small when K_3' is most important, then one obtains equation 244 when equation 241 is solved for K_3'.

$$K_3' = \frac{(3 - a') + (4 - a')\frac{1}{HK_4'}}{(a' - 2)H + (a' - 1)H^2K_2'} . \qquad (244)$$

Only rough approximations of K_4' and K_2' are necessary in evaluating K_3' in the region of $\underline{a}' = 2.5$.

However, both K_1' and K_2' are important for the region $\underline{a}'$ equal to less than 2. Therefore, K_1' and K_2' must be solved simultaneously from two points on the titration curve. If $\underline{H} = \underline{H}_1$ when $\underline{a}' = \underline{a}_1'$ and $H = H_2$ when $\underline{a}' = \underline{a}_2'$, and the terms of numbers 1 and 4 are ignored in equation 241 since they are extremely small when K_1' and K_2' are important, then one obtains the following two equations:

$$a_1'H_1^2K_1'K_2' + (a_2' - 1)H_2K_2' + (a_1' - 2) + (a_1' - 3)\frac{1}{H_1K_3'} = 0 \tag{245}$$

$$a_2'H_2^2K_1'K_2' + (a_2' - 1)H_2K_2' + (a_2' - 2) + (a_2' - 3)\frac{1}{H_2K_3'} = 0 \tag{246}$$

The values of K_2' and $K_1'K_2'$ are obtained by solving simultaneously equations 245 and 246, and K_1' is obtained from the quotient of $K_1'K_2'$ and K_2. In order to solve for K_1' and K_2' in this way, the points must be at the same ionic strength. Since the term containing K_3' has only a very small effect, only a rough approximation of K_3' is necessary.

Results

The values of K_1', K_2', K_3', and K_4' calculated for the three ionic strengths from the titration curves are given in Table 6. The Debye-Hückel Theory predicts that a plot of log K' versus the square root of the ionic strength should give almost a straight line at low ionic strengths. Therefore, each of the four apparent constants were plotted in this fashion so that these constants could be obtained for any ionic strength in this range (see Table 7). These constants will be needed for calculations indicated in the next section of the thesis.

Table 6. Stability constants of EDTA

K_i'	a'	-log H	μ	log K_i'
K_4'	3.2965	9.889	0.123	10.264
K_4'	3.411	10.114	0.123	10.274
K_4'	3.482	10.240	0.123	10.272
K_4'	3.309	10.080	0.0419	10.430
K_4'	3.3625	10.175	0.0419	10.420
K_4'	3.492	10.410	0.0419	10.424
K_4'	3.149	9.89	0.0115	10.675
K_4'	3.195	10.040	0.0115	10.683
K_4'	3.249	10.200	0.0115	10.705
K_3'	2.3965	5.995	0.107	6.176
K_3'	2.496	6.145	0.107	6.149
K_3'	2.596	6.305	0.107	6.135
K_3'	2.4005	6.155	0.0389	6.345
K_3'	2.5005	6.330	0.0389	6.328
K_3'	2.6005	6.495	0.0389	6.318
K_3'	2.402	6.266	0.0111	6.438
K_3'	2.5015	6.421	0.0111	6.418
K_3'	2.601	6.06	0.0111	6.424
K_2'	1.508	2.880	0.107	2.678
K_1'	0.875	2.290	0.102	2.115
K_2'	1.508	2.880	0.107	2.685
K_1'	0.847	2.530	0.102	2.109
K_2'	1.442	2.940	0.0303	2.827
K_1'	0.760	2.315	0.0318	2.226
K_2'	1.398	2.986	0.0057	2.959
K_1'	0.720	2.321	0.0080	2.218

Table 7. Stability constants of EDTA

$\sqrt{\mu}$	log K'_1	log K'_2	log K'_3	log K'_4
0.100	2.24	2.92	6.45	10.70
0.200	2.19	2.81	6.32	10.44
0.300	2.12	2.70	6.18	10.27

APPARENT EQUILIBRIUM CONSTANTS

The true thermodynamic formation constants of the complex ions and molecules in the solution phase are not known. These constants would be products and ratios of the activities of the various ions and molecules occurring in the solution phase. Since the activity of an ion or a molecule is the product of the activity coefficient and the concentration of the species involved, the true equilibrium constant may be divided by the products and ratios of the activity coefficients for a solution of given composition and concentration, and thus a new constant will be obtained which is known as the apparent equilibrium constant. This can be readily determined experimentally from the right hand side of the equation which involves only the concentrations. For very dilute solution, the activity coefficients change with ionic strength in a known manner. Therefore, the apparent equilibrium constant for a given ionic strength may be calculated from the thermodynamic constant or the apparent constant at some other low ionic strength by using the Debye-Hückle Theory.

In this thesis, the batch equilibrium experiments were designed to determine the apparent equilibrium constants in the concentration range which was likely to occur in the band elutions. (See Table 8 for the definitions of the various apparent equilibrium constants.) While the data obtained were not sufficient to determine the true thermodynamic constants or to give plots of activity coefficients versus ionic strength, the data does indicate that the elution procedure with the flat type elution curves might be a powerful tool to determine the activity coefficients and the thermodynamic constants of complex ions and complex molecules. The same arguments apply to the apparent ion-exchange constants between the ions on the resin and the ions in the solution. In this case, the activity coefficients of the ions on the resin should be very dependent on the equivalent concentration and composition of the resin phase. As the hydrated ions go into the resin, they take with them various amounts of water due to osmotic pressure. Therefore, the amount of water in the resin is sensitive to this equivalent ionic composition. Also, due to the cross-linking in the resin network, only a certain amount of water can enter so that the solution concentration of ions in the resin is high, being of the order of 6 to 8 normal. As is well known, solutions of high ionic strength have a marked effect on the activity coefficients. All these factors, osmotic pressure, high concentration, etc., will make the apparent equilibrium constants very sensitive to the resin composition. Here, again, the elution technique with flat type elution curves should provide a powerful tool for solving the very difficult problems connected with determining the activity coefficients of ions in the resin and the true thermodynamic constants of the resin-solution exchange.

Since there are three independent variables in both the copper-ammonium-hydrogen band and the neodymium-ammonium-hydrogen band, for example, μ, E_H, and E_{NH_4} or E_M (where M represents the metal ion), the apparent ion-exchange constants may be a function of at least three variables. Since the copper-hydrogen band has two independent variables, the apparent ion-exchange constant K'_E in this band may be a function of at least two variables. Due to the limited range of conditions under which the constants are determined in this thesis and to the experimental error, it is generally only possible to find one variable which has much of an effect on each of the apparent ion-exchange constants. The K'_F was found to be mainly a function of the equivalent fraction of hydrogen ion on the resin in both the copper-ammonium-hydrogen band and the neodymium-ammonium-hydrogen band. The K'_D was found to be mainly a function of the ionic strength.

The concentration of the neodymium ion was so small that it was not possible to calculate its concentration from the experimental data obtained; however, it was possible to eliminate this difficulty by determining the apparent constant K'_I/K'_G ratio from the data. This eliminates the necessity of knowing the concentration of the neodymium ion since it has been eliminated from the only two equilibrium equations involving this ion and since the neodymium ion concentration may be set equal to zero in the charge balance and the material balance equations without making too much of an error.

The values of these various apparent constants are given in Tables 9, 10, and 11. The method used in calculating these constants from the equations given in the theoretical section is discussed in the Appendix. Although there is some difference in the constants determined by the elution and the batch equilibrium experiments, these differences can easily be accounted for by the experimental errors in determining the concentrations and by the simplifying assumptions made in the calculations.

It is possible to predict quite closely the composition of the various phases under equilibrium conditions without performing an elution from the ion-exchange elution theory providing one can estimate or determine roughly the apparent equilibrium constants involved in the equations. Thus, beds which are near the equilibrium composition can be prepared so that it requires much less time to achieve the true equilibrium conditions.

Table 8. Apparent equilibrium constants

Copper-ammonium-hydrogen and copper-hydrogen bands		Neodymium-ammonium-hydrogen band	
K_i'	Definition	K_i'	Definition
K_A'	$\frac{CuY}{Cu \times Y}$	K_G'	$\frac{NdY}{Nd \times Y}$
K_B'	$\frac{HCuY}{H \times CuY}$	K_H'	$\frac{HNdY}{H \times NdY}$
K_C'	$\frac{H_2CuY}{H \times HCuY}$	K_I'	$\frac{(NH_4)^3 \, E_{Nd}}{Nd \, E^3_{NH_4}}$
K_D'	$\frac{(NH_4)^2 \, E_{Cu}}{Cu \, E^2_{NH_4}}$		
K_E'	$\frac{H^2 \, E_{Cu}}{Cu \, E^2_H}$		

K_i	Definition
K_F'	$\frac{H \, E_{NH_4}}{NH_4 \, E_H}$
K_1'	$\frac{H_4Y}{H \times H_3Y}$
K_2'	$\frac{H_3Y}{H \times H_2Y}$
K_3'	$\frac{H_2Y}{H \times HY}$
K_4'	$\frac{HY}{H \times Y}$

Table 9. Apparent equilibrium constants in the copper-ammonium-hydrogen band

	μ	K'_B	K'_C	E_{Cu}	E_{NH_4}	E_H	K'_o	K'_F	K'_E
Elution 29	0.0356	1330	(147)	0.8436	0.1510	0.0053	1.96	1.94	7.4
E-3	0.0311	1520	(150)	0.5882	0.4041	0.00771	2.62	1.25	4.1
E-4	0.0430	1340	(145)	0.5500	0.4479	0.00209	2.66	0.944	2.4
E-5	0.0432	1420	(145)	0.6033	0.3889	0.00782	2.50	1.17	3.4
E-6	0.0334	1410	(150)	0.5857	0.4079	0.00641	2.92	1.19	4.15
E-7	0.0151	1620	(162)	0.5959	0.3862	0.01796	3.97	1.58	9.9
E-8	0.0335	1510	(150)	0.5746	0.4192	0.00622	2.73	1.17	3.7

Table 10. Apparent equilibrium constants in the copper-hydrogen band

	μ	$K'_A \times 10^{-19}$	K'_B	K'_C	E_{Cu}	E_H	K'_E
Elution 27	0.0082	3.46	(1730)	170	0.5275	0.4725	6.3
Elution 28	0.0068	3.82	(1760)	171	0.6064	0.3936	7.62
Elution 29	0.0090	3.28	(1720)	169	0.7583	0.2417	10.43

Table 11. Apparent equilibrium constants in the neodymium-ammonium-hydrogen band

	μ	$K'_G \times 10^{-17}$	K'_H	E_{Nd}	E_{NH_4}	E_H	K'_F	$K'_I/K'_G \times 10^{16}$	K'_I
Elution 27	0.0173	1.89	55	0.7416	0.2512	0.00716	1.43	2.06	38.6
Elution 28	0.0153	2.09	39	0.6638	0.3254	0.01073	1.52	1.93	40.4
E-9	0.0151	2.11	52	0.74125	0.25034	0.00841	1.025	2.18	45.8
E-10	0.0148	2.15	48	0.70177	0.28740	0.01083	1.12	2.08	44.6
E-11	0.0142	2.23	65	0.66225	0.32469	0.01306	1.19	2.02	44.8

DISCUSSION OF RESULTS

According to the simple theory a buffered EDTA eluant could be used to drive a rare-earth band down a pure hydrogen retaining bed, but in practice this is not feasible since the low solubility of the H_4Y^o formed in the boundary II region causes that acid to precipitate and plug the column. It was shown theoretically for each eluant that a homogeneous copper-hydrogen retaining bed was superior to the pure hydrogen bed. However, even here there was a tendency for the H_4Y^o to precipitate in the boundary region. On the other hand, if a narrow copper-ammonium-hydrogen band was inserted between the rare-earth band and the copper-hydrogen retaining bed, this precipitation could be prevented. With a retaining bed of copper-hydrogen of the right composition for a given eluant, this inserted copper-ammonium-hydrogen region would come to equilibrium and would neither grow nor shrink as the bands progress down the column. Elutions 27 and 28 demonstrated that these conditions could be achieved. Flat type elution curves were obtained, the length of the copper-ammonium-hydrogen band did not change perceptibly, and the rate of band travel indicated that no appreciable leak throughs occurred through the boundary regions except the steady leak through of $\bar{H}_T$ and $\bar{Y}_T$.

Theory further showed that for a given eluant, a considerable range of compositions of the copper-hydrogen retaining bed could be used. For each composition, a definite leak of ammonium in boundary I and copper and hydrogen in boundary III would be established and the copper-ammonium-hydrogen band of fixed composition would grow at just the rate determined by these transports. Elution 29 demonstrated that this condition could be achieved since again flat type elution curves were obtained and the transports were approximately as calculated (see the Appendix).

In the theory it was assumed that no EDTA entered the resin or remained in the band. Actually, any neutral species of EDTA such as H_4Y^o, $HNdY^o$, or H_2CuY^o could enter the resin phase and would be expected to partition themselves between the dilute aqueous phase of the eluate and the concentrated aqueous phase of the resin. However, the concentration of these ions in the dilute aqueous phase is very low so that the amount in the concentrated resin phase should not be very large.

Also, the EDTA molecule has two nitrogen atoms which act as hydrogen acceptors and the molecular species H_5Y^+, H_6Y^{+2}, H_2NdY^+, H_3CuY^+, etc. may have appreciable stability constants. If they do, these ions should be absorbed in the resin in the high acid regions. If such ions exist, they would have to be taken into account in the theory. This can be done but was not done in this thesis since experiments indicate that any such effect would be very small, probably less than the experimental accuracy of determining some of the concentrations. If the effect exists, the Y_T should vary slightly from band to band. Actually, a small variation was noted, but it was only slightly greater than the experimental errors. Since this variation could be caused by other factors, it was felt that the data did not warrant the calculation of such an effect. The simple theory was able to predict the results to within a few per cent. Thus, it was felt that a careful study of this effect should be reserved for later investigations.

In elution 29, it was noticed that, after the rare-earth eluate had remained in the flasks for a day or two, a slight precipitate formed in the bottom of the flasks. This indicated that the $\bar{Y}_T$ in eluant was probably a little high for the experiment and that some of the molecules in solution were in a supersaturated state. If this were true, there may be a slight invisible precipitation occurring in the rare-earth band; this would cause the EDTA to accumulate in the column and cause a slight variation of Y_T throughout the column. In the future investigations, these minor side effects will be studied. Future experiments should have lower concentrations of $\bar{Y}_T$ in the eluant.

Attention should also be called to the fact that in elution 29 the top third of the elution curve was not flat. This could be caused by the fact that part of the band had not quite reached the equilibrium state. This could be corrected by eluting the bands much further down the column. On the other hand, the slight trailing off of the elution curve in the copper-ammonium-hydrogen band might be explained as due to a rapid reaction of copper forming a one to one complex with EDTA as neodymium is deposited on the resin. This is followed by a slow exchange of ammonium ion in solution with copper ion on the resin which increases the cupric ion concentration to its equilibrium value. If this were the case, then the steady state boundary region would be longer and have an odd shape. Longer elutions could settle this problem and should be studied in further investigations.

In addition, it might be interesting to determine the maximum positive and negative transport possible under various conditions. It might be desirable to know why these exist and how they might be estimated.

SUMMARY

It was shown that flat elution curves were maintained with constant length rare-earth bands using either copper-ammonium-hydrogen or copper-hydrogen retaining beds. However, when the copper-hydrogen retaining band was used, some precipitation occurred at the lower boundary region of the rare-earth band. When the copper-ammonium-hydrogen band was used, a longer time was required to achieve equilibrium in this band. When a narrow copper-ammonium-hydrogen band was used, between the rare-earth and the copper-hydrogen bed, the precipitation was prevented and the "flat" equilibrium type elution curves were obtained. It was demonstrated that when a final retaining bed of the proper composition is used with a given eluant, then the interposed band and the rare-earth band maintains a constant length. In addition, it was demonstrated that, when the final retaining bed was not compatible with the eluant, then the flat type elution curves were maintained with the interposed band growing in length and the rare-earth band remaining constant in length.

A theory was developed for this elution system which is in agreement with these experimental results. This theory shows that if the composition of the eluant, the composition of the final retaining bed, and the apparent equilibrium constants involved in the system are known, then the equilibrium, the material balance, and the charge balance equations can be

used to calculate the composition of the various phases in the equilibrium system and to calculate the mass transports that occur at the band boundaries. This theory further showed that for a given eluant, a considerable range of copper-hydrogen retaining-bed compositions could be used. For each composition, a definite transport of ammonium in the upper boundary of the interposed bed and of copper and hydrogen in the lower boundary would be established and the copper-ammonium-hydrogen band of fixed composition would grow at the rate determined by these transports.

Several batch equilibrium experiments were performed in order to obtain apparent equilibrium constants which could be compared with the apparent constants obtained from the above indicated elution experiments. In addition, the four stability constants of EDTA were determined for the three ionic strengths, 0.1, 0.04, and 0.01. These apparent constants were used in the elution and batch equilibrium calculations.

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APPENDIX

Evaluation of Apparent Equilibrium Constants

The equilibrium constants essential for the description of the copper-ammonium-hydrogen band are more easily evaluated than those for any of the other bands. Therefore, the calculation of the apparent equilibrium constants with the data from the copper-ammonium-hydrogen band (region 3) will be discussed first.

Copper-ammonium-hydrogen band

The K_B' and K_C' are important in determining the composition of the eluate (see equations 118 and 121). The K_B' can be more accurately determined in the high pH range of the eluate from the copper-ammonium-hydrogen band while K_C' can be determined more readily in the higher acidic range of the copper-hydrogen band.

When CuY is eliminated between equations 168 and 170, the following equation is obtained:

$$K_B' = \frac{b}{H\,(1 - b) + HK_C'(2 - b)} \qquad (247)$$

where

$$b = \frac{H_T - H}{Y_T}\ . \qquad (248)$$

When $K_A' \times Cu \times Y$ is eliminated between equations 126 and 131, the following equation is obtained:

$$K_C' = \frac{1 - c}{H^*(2c - 1)} + \frac{1}{K_B'(2c - 1)(H^*)^2} \qquad (249)$$

where $$c = \frac{Cu_T^* - Cu^*}{H_T^* - H^* - B^* \times Y^*} \qquad (250)$$

(see equations 269 and 267).

It is necessary to calculate the variation of K_C' with ionic strength using the Debye-Hückel theory because there are not enough points to establish this variation (70); thus:

$$K_C = \frac{H_2CuY}{H \times HCuY} \; \frac{\gamma_{H_2CuY}}{\gamma_H \times \gamma_{HCuY}} = K_C' \; \frac{1}{\gamma_H \times \gamma_{HCuY}} \qquad (251)$$

and $$\log K_C' = \log K_C + \log \gamma_H + \log \gamma_{HCuY} \qquad (252)$$

where $$\log \gamma_i = - \frac{0.5085(Z_i)^2\sqrt{\mu}}{1 + 0.328\, a_i\sqrt{\mu}} \, . \qquad (253)$$

Therefore, $$\log K_C' \cong \log K_C - \frac{1.017\sqrt{\mu}}{1 + 2.6\sqrt{\mu}} \, , \qquad (254)$$

when $a_i \cong 8$ (an estimate). The symbols γ_i and Z_i represent the activity coefficient and charge, respectively, of the ion <u>i</u>. The ionic strength is represented by the symbol μ.

Since there are enough points to evaluate the variation of K_B' with ionic strength, the a_i may be determined from the experimental results:

$$\log K_B' = \log K_B - \frac{0.5085(4)\sqrt{\mu}}{1 + 0.328\, a_i\sqrt{\mu}} \, . \qquad (255)$$

The ionic strength of the eluate in the copper-ammonium-hydrogen band is given by the following equation:

$$\mu = \frac{1}{2}(NH_4 + 4Cu + H + HCuY + 4CuY) \ . \qquad (256)$$

The variable NH_4 may be eliminated by using equation 173, CuY by equation 167, and HCuY by equation 169; thus,

$$\mu = 3Y_T - 2(H_T - H) + Cu + H_2CuY \ . \qquad (257)$$

Since the value of H_2CuY is relatively small, only an extremely small error is made in approximating H_2CuY by the following equation (see equation 169):

$$H_2CuY = K'_C \times H \times HCuY \cong HK'_C(H_T - H) \ . \qquad (258)$$

Therefore, $\mu \cong 3Y_T - (2 - HK'_C)(H_T - H) + Cu_E \ . \qquad (259)$

The ionic strength in the copper-hydrogen band eluate is given by the following equation:

$$\mu = \frac{1}{2}(H^* + HCuY^* + 4CuY^* + 4Cu^* + H_3Y^* + 4H_2Y^*) \ . \qquad (260)$$

Eliminating HCuY using equation 127, gives the following equation:

$$\mu = H^* + CuY^* + 3Cu^* + H_2Y^* \ . \qquad (261)$$

The H_2Y^* may be ignored because it is very small. When H_4Y^*, H_3Y^*, and H_2Y^* are ignored in equation 131, a very good approximation for CuY^* is obtained:

$$\mu \cong H^* + \frac{H_T^* - H^*}{H^*K'_B + 2H^{*2}K'_CK'_B} + 3Cu^* \ . \qquad (262)$$

The constants log K_C, log K_B, a_1 were determined by finding those values which allow the equations 247, 249, 254, 255, 259, and 262 to give the best agreement with the experimental results. Thus,

$$\log K_B' = 3.38 - \frac{2.034\sqrt{\mu}}{1 + 4.0\sqrt{\mu}}\,, \qquad (\mu = 0.015 - 0.04)\ ; \qquad (263)$$

and

$$\log K_C' = 2.304 - \frac{1.017\sqrt{\mu}}{1 + 2.6\sqrt{\mu}}\,, \qquad (\mu = 0.007 - 0.01)\ . \qquad (264)$$

Unlike the apparent equilibrium constants for a solution, the apparent ion-exchange constant may be a function of several variables. Therefore, the constant must be determined under the same conditions as those in which the apparent constant is to be used. The apparent ion-exchange constants K_F', K_D', and K_E' (see equations 156, 154, and 108) are determined for the six equilibrium experiments and the copper-ammonium-hydrogen band in elution 29 (see Tables 1, 2, and 9).

Copper-hydrogen band

When equation 124 is subtracted from equation 126, the following equation is obtained:

$$Cu_T^* - Y_T^* = Cu^* - (H_4Y^* + H_3Y^* + H_2Y^*) = Cu^* - A^* \times Y^* \quad (265)$$

where $A^* = K_1'K_2'K_3'K_4'(H^*)^4 + K_2'K_3'K_4'(H^*)^3 + K_3'K_4'(H^*)^2$; (266)

thus,

$$Y^* = \frac{Y_T^* - Cu_T^* + Cu^*}{A^*}\ . \qquad (267)$$

Equation 131 may be written as follows:

$$H_T^* - H^* = (K_B'K_A'H^* + 2K_C'K_B'K_A'H^*2)Cu \times Y^* + B^* \times Y^* \qquad (268)$$

where $$B^* = 4K_1'K_2'K_3'K_4'(H^*)^4 + 3K_2'K_3'K_4'(H^*)^3 + 2K_3'K_4'(H^*)^2; \qquad (269)$$

thus, $$H_T^* - H^* = \frac{(K_BK_AH^* + 2K_CK_BK_AH^{*2})(Y_T^* - Cu_T^* + Cu^*)Cu^*}{A^*} + \frac{B^*(Y_T^* - Cu_T^* + Cu^*)}{A^*} . \qquad (270)$$

The equation above is quadratic with respect to Cu* and could be solved for Cu* if K_A' were known.

The Debye-Hückel equation relating K_A' and the ionic strength may be derived in the same manner as was indicated for the Debye-Hückel equation for K_C'. Then,

$$\log K_A' = \log K_A - \frac{0.5085(16)\sqrt{\mu}}{1 + 0.328\ a_1\sqrt{\mu}} . \qquad (271)$$

The log K_A' is known to be 18.8 at 0.1 ionic strength (62). The 0.328 a_1 was estimated to be 3.0; therefore, log K_A may be estimated in this manner, and

$$\log K_A' = 20.12 - \frac{8.15\sqrt{\mu}}{1 + 3.0\sqrt{\mu}} . \qquad (272)$$

The definition of the apparent ion-exchange constant was indicated previously as

$$K_E' = \frac{H^*\ E_{Cu}^*}{Cu^*\ (E_H^*)^2} . \qquad (273)$$

The values of this apparent constant were calculated from the data in Table 1 and are given in Table 10.

Neodymium-ammonium-hydrogen band

When equation 206 is subtracted from equation 204, the following equation results:

$$Y_T - Nd_T = H_4Y + H_3Y + H_2Y - Nd \ . \qquad (274)$$

Thus,
$$Y_E = A \times Y - Nd, \qquad (275)$$

and
$$Y = \frac{Y_E + Nd}{A} \ . \qquad (276)$$

Equation 206 may be written as follows:

$$Nd_T = Nd + (1 + HK'_H)NdY \ ; \qquad (277)$$

thus,
$$NdY = \frac{Nd_T - Nd}{1 + HK'_H} \ . \qquad (278)$$

Substitution of these values of Y and NdY into equation 208 gives the following equation:

$$H_T = H + \frac{HK'_H(Nd_T - Nd)}{1 + HK'_H} + C(Y_E + Nd) \qquad (279)$$

where
$$C = \frac{B}{A} = \frac{4K'_1K'_2K'_3K'_4H^4 + 3K'_2K'_3K'_4H^3 + 2K'_3K'_4H^2}{K'_1K'_2K'_3K'_4H^4 + K'_2K'_3K'_4H^3 + K'_3K'_4H^2} \ . \qquad (280)$$

Thus,
$$K'_H = \frac{d}{H(1 - d)} \qquad (281)$$

where
$$d = \frac{H_T - H - C(Y_E + Nd)}{Nd_T - Nd} \ . \qquad (282)$$

Generally Nd is smaller than experimental error, and K'_H may be calculated from the data available (Tables 1 and 4). If necessary K'_H may be corrected later for the small effect of the neodymium ion, Nd, by substituting its calculated value.

When Nd is eliminated between equations 191 and 199, the following equation is obtained:

$$\frac{K_I'}{K_G'} = \frac{(NH_4)^3 \times E_{Nd} \times Y}{(E_{NH_4})^3 \times NdY} \quad . \tag{283}$$

When Y and NdY are eliminated from the above equation by means of equations 278 and 276, the following equation is obtained:

$$\frac{K_I'}{K_G'} = \frac{(NH_4)^3\ E_{Nd}\ (1 + HK_H')(Y_E + Nd)}{(E_{NH_4})^3(Nd_T - Nd)A} \quad . \tag{284}$$

The ratio of these two constants, K_I'/K_G', may be calculated from the data available either by ignoring Nd or by correcting for it.

The apparent equilibrium constant K_G' may be expressed as a function of ionic strength by using the Debye-Hückel theory (see equation 199); thus,

$$\log K_G' = \log K_G - \frac{0.5085(24)\sqrt{\mu}}{1 + 0.328\ a_i\sqrt{\mu}} \quad . \tag{285}$$

The value of K_G' is known for 0.1 ionic strength to be 16.48 (62). The 0.328 a_i is estimated to be 3.2; therefore, log K_G may be estimated in this manner. Thus,

$$\log K_G' = 18.4 - \frac{12.2\sqrt{\mu}}{1 + 3.2\sqrt{\mu}} \quad . \tag{286}$$

The ionic strength of the eluate in the neodymium-ammonium-hydrogen band may be written as follows:

$$\mu = \frac{1}{2}(NH_4 + H + 9Nd + NdY + H_3Y + 4H_2Y) \ . \qquad (287)$$

When equation 210 is used to eliminate NdY and H_3Y, the following equation is obtained:

$$\mu = NH_4 + H + H_2Y + 6Nd \ . \qquad (288)$$

Equation 208 may be written as follows (see equations 34 and 37):

$$H_T = H + HNdY + (2 + 3K_2' \times H + 4K_2'K_1'H^2)H_2Y \ . \qquad (289)$$

Since HNdY is small, it may be approximated very well by the following equation:

$$HNdY = HK_H' \ NdY \cong HK_H' \ Nd_T \ . \qquad (290)$$

When equation 289 is solved for H_2Y and this value is substituted into equation 288, the following equation is obtained:

$$\mu = NH_4 + H + \frac{H_T - H - HK_H' \ Nd_T}{2 + 3K_2'H + 4K_2'K_1'H^2} + 6Nd \ . \qquad (291)$$

When NdY and Y are eliminated from equation 199 by using equations 278 and 276, the following equation is obtained for Nd:

$$Nd = \frac{(Nd_T - Nd)A}{K_G'(Y_E - Nd)(1 + HK_H')} \ . \qquad (292)$$

The apparent constants K_H', K_I'/K_G', K_I', and K_F' were calculated from the data in Tables 1 and 3 and are given in Table 11. The K_I' calculated at the ionic strengths of approximately 1.0 and 0.1 were 166 and 240, respectively, when E_{Nd} is 0.70 (19). Therefore, these results show an increase in K_I' with decreasing ionic strength. The value of K_I' of 38 to 46 at an ionic strength of 0.015-0.017 and for E_{Nd} equal to approximately 0.70 (Table 10) shows that K_I' decreases with decreasing ionic strength in this lower ionic strength range. However, since K_G' is only approximate and K_I' is calculated from K_I'/K_G' and K_G', there is some uncertainty in K_I' given in Table 10, but probably not enough for K_I' to be increasing with decreasing ionic strength in this lower ionic-strength range. Levin et al. (20) have results which are in agreement with the above behavior of K_I'. At the lower ionic strengths, apparent constants of this type showed a pronounced decrease with decreasing ionic strength.

Testing of the Interdependence of Transports in the Various Boundaries

Since the three elution experiments seem to fulfill the conditions specified by the theory, it was decided that the transport of ammonium would be calculated from somewhat independent sets of data in order to further test the validity of the theory. The transports are very sensitive functions of the experimentally determined concentrations, and any errors in these experimentally determined quantities will be magnified in the transport calculations.

The value of $T_{NH_4}^{I}$ may be calculated from the resin and solution composition of the neodymium-ammonium-hydrogen band (see equations 181, 182, and 185); that is,

$$N_{I} = \frac{3Nd_{T}}{E_{Nd} + 3Nd_{T}f} = \frac{NH_4 - T^{I}_{NH_4}}{E_{NH_4} + NH_4 f} \; ; \qquad (293)$$

thus,

$$T^{I}_{NH_4} = NH_4 - \frac{3Nd_{T}(E_{NH_4} + NH_4 f)}{E_{Nd} + 3Nd_{T}f} \; . \qquad (294)$$

The value of $T^{II}_{NH_4}$ may be calculated from the resin and solution compositions of the copper-ammonium-hydrogen band (see equations 145 and 147); that is,

$$N_{II} = \frac{2Cu_{T}}{E_{Cu} + 2Cuf} = \frac{NH_4 - T^{II}_{NH_4}}{E + NH_4 f} \; , \qquad (295)$$

and thus,

$$T^{II}_{NH_4} = NH_4 - \frac{2Cu_{T}(E_{NH_4} + NH_4 f)}{E_{Cu} + 2Cuf} \; . \qquad (296)$$

Also, the expected value of $T^{II}_{NH_4}$ may be calculated using equation 178; then,

$$\frac{T^{II}_{NH_4}(E_{Cu} + 2Cu_{T}f)}{E_{NH_4} + NH_4 f} = \frac{E^{*}_{Cu} + 2Cu^{*}_{T}f}{E^{*}_{H} + h^{*}_{T}f}\left(h^{*}_{T} + T^{II}_{NH_4} \times \frac{E_{H} + h_{T}f}{E_{NH_4} + NH_4 f}\right) - 2Cu^{*}_{T} \; . \qquad (297)$$

In the case of elutions 27 and 28, the short interposed copper-ammonium-hydrogen band which did not grow was too small to allow an accurate determination of its composition. Since $T^{II}_{NH_4}$, however, is primarily determined by the eluant composition and the solution and resin compositions of the copper-hydrogen band, the accuracy of evaluting $T^{II}_{NH_4}$ is not greatly decreased.

Table 12 shows the results obtained by substituting the data from elutions 27, 28, and 29 into the three equations 294, 296, and 297 (see Table 1). The value of f has been found to be approximately 0.15 liters of eluate per equivalent of resin. The values of T_{NH_4} calculated for elution 27 and elution 28 are in good agreement and show no appreciable transport.

Table 12. The calculated values of T_{NH_4}

Equations	Elution 27	Elution 28	Elution 29
294	+0.00024	-0.00005	+0.00710
296	--	--	+0.00674
297	+0.00017	+0.00007	+0.00651[a]

[a] If the value of h_T^* used is calculated on the basis of $\bar{H}_T$ expected from the value of H_T in the copper-ammonium-hydrogen band, then the calculated value of $T_{NH_4}^{II}$ is 0.00685.

The value of T_{NH_4} for elution 29 shows a definite transport across the predicted boundaries, and agreement between the values calculated in different ways is as good as one might expect from the accuracy of the experimental data used and the simplifying assumptions used in the calculations from the theory.